Cluster Expansion of the Wave Function. Ionization and Excitation Spectra of NO Radical Studied by the SAC and SAC-CI Theory

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Abstract

The ionization spectrum of the NO radical is studied from outer- to inner-valence regions by the SAC and SAC-CI theories. The excited states of the NO radical are also calculated. The theoretical ionization spectrum has reproduced well the general features of the experimental spectra observed by ESCA and (*e*, 2*e*) spectroscopies. We have given for the first time the assignments of all the ionization peaks observed in both the outer- and inner-valence regions. The ionization spectrum of the doublet radical involves some interesting complexity in comparison with that of closed-shell molecules.

1. Introduction

Studies of electron correlations of molecules in open-shell and excited states are current topics in theoretical quantum chemistry. It is generally recognized that electron correlation is very important for adequate descriptions of these states [1]. In recent years, we have developed cluster expansion theories, called SAC (symmetry-adapted-cluster) theory [2] and SAC-CI theory [3], for the studies of electron correlations in ground and various excited states of molecules. The theories have been applied to singlet and triplet excited states, ionized states, and electron attached states of molecules such as H_2O [2b,4], CH_2 [2b], H_2CO [5], CO_2, and N_2O [6]. These states are essentially one-electron excited states. We have also applied the theory to the analysis of the satellite peaks of inner-valence ionizations which involve two-electron simultaneous ionization–excitation processes. We have studied the ionization spectra of H_2O [7], CO_2, N_2O [6], CS_2, and COS [8]. We have also studied spin- and electron-correlation effects on the hyperfine splitting constants of several organic doublet radicals [9,10].

In this article we report the result of applications of the SAC and SAC-CI theory to the ionization and excitation spectra of the NO radical. The Hartree–Fock configuration of the NO radical is

$$(\text{core})^4\ (1\sigma)^2\ (2\sigma)^2\ (3\sigma)^2\ (1\pi)^4\ (2\pi)^1. \qquad (1)$$

By ionization of an electron, we obtain the closed-shell ground state of the NO cation and various singlet and triplet excited states of the NO cation. The number

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of states generated by ionization of the doublet radical, NO, is larger than that generated by ionization of a similar closed-shell molecule, e.g., CO. Consequently, the ionization spectrum of the NO radical [11–16] is more complicated than that of CO [11,12,14].

Recently, Brion and Tan [15] and Fantoni et al. [16] reported the ionization spectra of the NO radical in the binding energy range up to 60 eV by dipole and binary (e, $2e$) spectroscopies, respectively. In the upper side of Figure 1, we have reproduced the spectrum reported by Brion and Tan [15]. The spectrum in the lower side of Figure 1 is the MgK_α ESCA spectrum originally reported by Siegbahn et al. [11]. For the energy range 10–20 eV, these spectra are in accord with the high resolution photoelectron spectrum reported by Turner et al. [12],

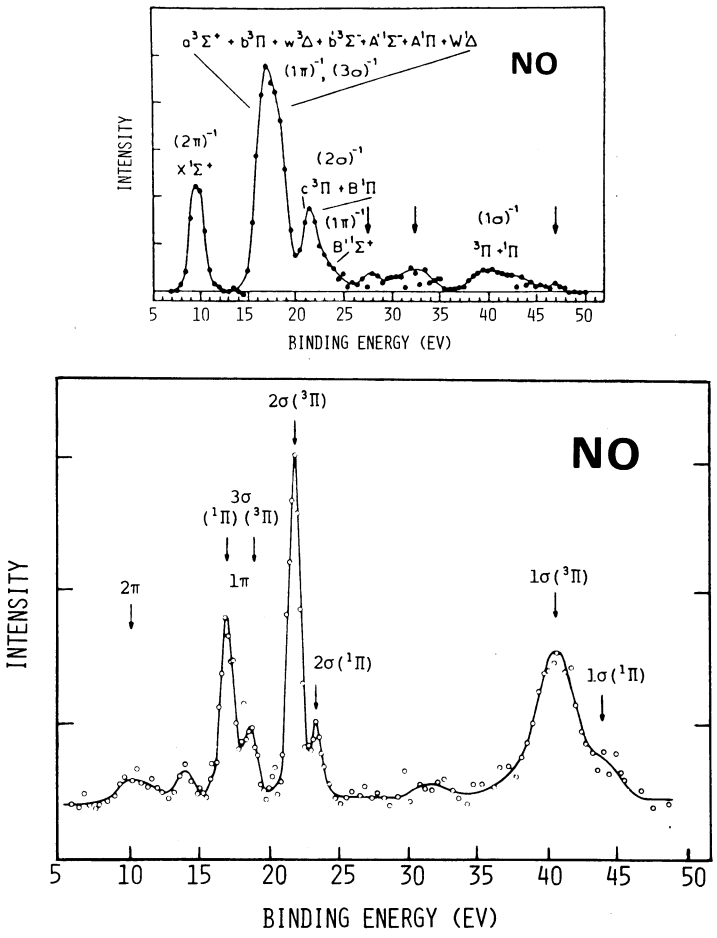
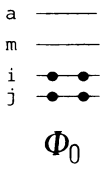


Figure 1. Experimental ionization spectra of the NO radical obtained by Brion and Tan [15] with dipole (e, $2e$) spectroscopy (upper) and by Siegbahn et al. [11] with ESCA spectroscopy (lower).

Edquist et al. [13], and Kimura et al. [14]. The assignments of these outer-valence ionization peaks are almost established, except for an ordering between the $^1\Pi$ and $^3\Sigma^-$ states [11,14]. In the inner-valence region, 25–50 eV, however, the (*e*, 2*e*) spectrum shows several broad peaks in the ranges 25–35 and 45–50 eV, which are unexpected from a simple molecular orbital picture. Brion and Tan reported that these small peaks (indicated by arrow in Fig. 1) consistently appear at energies of ca. 28, 33, and 47 eV. A small peak in the ESCA spectrum at ca. 31 eV should be due to the same origin. From the analogy of the studies of Cederbaum, Domcke, and co-workers [17] and ours [5–7] for ionization spectra of closed-shell molecules, we may expect a final-state correlation effect as a source of these peaks. However, for open-shell molecules, the nature of the final-state correlation should be different from that for closed-shell molecules. It may involve interesting electronic states which are seldom observed by other means.

The final-state correlation in open-shell radicals has some interesting complexity. Let us assume that the satellite peaks are due to a mixing of simultaneous ionization–excitation (shake-up) processes to an ordinary single ionization process. For open-shell radicals, the final ionic state may be expressed by a sum of the configurations as shown in Figure 2.

The configuration Φ_1 represents a single excitation process. The intensity of the peak is roughly proportional to the weight of the configuration, C_1^2, if the initial-state correlation is small. The configurations Φ_2 and Φ_3 represent two different kinds of shake-up configurations. The former (Φ_2) involves an ionization or excitation from a singly occupied orbital ϕ_m but the latter (Φ_3) does not. When we consider these configurations as excited states of the closed-shell ground state of the cation, whose main configuration is



Φ_0

the configurations Φ_1 and Φ_2 are both singly excited configurations of the Φ_0 and the configuration Φ_3 is a doubly excited configuration of the Φ_0. Since the

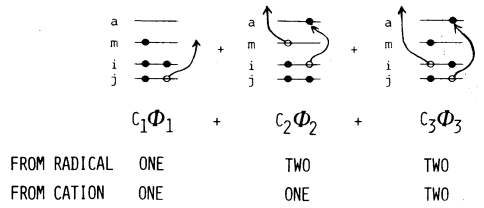


Figure 2. Schematic representation of the important configurations in the study of ionization spectra of open-shell radicals. One or two denotes the number of electrons involved in the process.

doubly excited state of the closed-shell molecule is seldom observed, partly because of its high energy and partly because of the forbidden nature of the selection rule with the ground state, it is interesting to analyze the ionization spectrum of the NO radical to see whether such a state is certainly involved or not. The role of the singly excited configuration Φ_2, which is present only for ionizations of open-shell radicals, is also of interest.

Recently, Grein and Kapur [18] reported a CI study of low-lying excited states of the NO radical. They also gave a complete review of the studies of excited states. Here, we will also report SAC-CI calculations of the low-lying Rydberg excited states of the NO radical.

2. Theoretical Background

Theories of the SAC and SAC-CI expansions have been given previously in detail [2, 3]. The SAC wave function is given by

$$\Psi_g = \mathbb{O} \exp\left(\sum_I C_I S_I^\dagger\right)|0\rangle, \tag{2}$$

where $\mathbb{O}$ is a symmetry projector and $S_I^\dagger$ a symmetry-adapted-cluster generator. The operator $S_I^\dagger$ should be symmetry adapted because of the nonlinear nature of the expansion [2]. The projector $\mathbb{O}$ is unnecessary for closed-shell molecules, as it is in this article. Like an ordinary cluster expansion, this expansion includes self-consistency as clearly seen from Thouless theorem [19] and multiple effects of electron correlation as clearly shown by Sinanoglu, Cizek, Paldus, and others [20]. Cluster expansion is then relatively insensitive to the choice of the reference wave function [21]. The SAC expansion is suitable for both closed- and open-shell molecules and excited states [2,10]. The difference of the SAC expansion from an ordinary cluster expansion was shown previously [2a].

When we apply the variational principle to the SAC wave function, we obtain the generalized Brillouin theorem

$$\langle\Psi_g|(H - E_g)S_I^\dagger|\Psi_g\rangle = 0. \tag{3}$$

Of course, the wave function is also solved nonvariationally by requiring that the Schrödinger equation is satisfied within the space of the linked operators,

$$\begin{aligned}\langle 0|(H - E_g)|\Psi_g\rangle &= 0,\\ \langle 0|S_I(H - E_g)|\Psi_g\rangle &= 0.\end{aligned} \tag{4}$$

Generally, the nonvariational solution is easier than the variational one [3b].

The SAC-CI theory is built on the SAC theory as follows [3]. We define the excited functions $\{\Phi_K\}$ as

$$\Phi_K = \mathcal{P} R_K^\dagger \Psi_g, \tag{5}$$

where $\mathcal{P}$ is a projector $\mathcal{P} = 1 - |\Psi_g\rangle \langle\Psi_g|$ and $R_K^\dagger$ is a symmetry-adapted excitation, ionization, or electron attachment operator depending on the nature of the excited state under consideration. For the excited state with the same symmetry as the ground state Ψ_g, $R_K^\dagger$ in Eq. (5) and $S_I^\dagger$ in Eq. (2) denote, in principle, the same set of operators. From Eq. (3), we see that the excited functions $\{\Phi_K\}$ satisfy the relations,

$$\begin{aligned} \langle\Phi_K|\Psi_g\rangle &= 0, \\ \langle\Phi_K|H|\Psi_g\rangle &= 0. \end{aligned} \tag{6}$$

These are the necessary conditions for the excited state to have to satisfy [22]. Thus, the functions $\{\Phi_K\}$ span the space for excited states, so that we describe the excited state Ψ_e by a linear combination of the functions $\{\Phi_K\}$ as

$$\Psi_e = \sum_K d_K \Phi_K. \tag{7}$$

This is a SAC-CI expansion. The coefficient d_K can be solved either variationally or nonvariationally [3b]. The latter solution involves a diagonalization of a nonsymmetric matrix, which can be performed by extending the Davidson's algorithm [23] to a nonsymmetric case [24].

We emphasize that the SAC theory gives not only an accurate wave function for the state under consideration, but also prepares the subspace which spans the space for excited states. Strictly speaking, this is valid only for variational solutions. However, so long as the cluster expansion theory is accurate enough, the difference of the two types of solutions should be small.

The SAC-CI expansion is expected to be more rapidly convergent than an ordinary CI expansion because it is based on the excited functions $\{\Phi_K\}$ which satisfy the necessary conditions for excited states, and because it starts from the ground-state electron correlation as seen from Eq. (5). Since excitations and ionizations are only one- or two-electron processes, most parts of the electron correlation should be similar between ground and excited states. This expansion includes also a spirit of multireference CI, i.e., correlation calculations starting from important multireference configurations [25], through the unlinked terms of Eq. (7). There, we use the ground state correlations as being transferable.

As theories related to the SAC-CI theory, we refer to the theories presented independently in the same year, 1978, by Paldus et al. [26] and by Ohmine et al. [27]. Although these theories are different, especially the renormalized CI method by Ohmine et al. is not strictly a cluster expansion theory, they have some physical idea in common, namely, transferability of electron correlation between ground and excited states.

The SAC and SAC-CI theories have some analogy to the Hartree–Fock and HF–SECI method in their theoretical framework [3a]. Table I shows that. For the ground state, the HF equation is just equivalent with the Brillouin theorem with respect to a *single* excitation operator $s_i^\dagger$, while the SAC equation (variational) is

TABLE I. Analogy in the theoretical framework between HF, HF-SECI theory and SAC, SAC-CI theory.

	HF, HF-SECI	SAC, SAC-CI
GROUND	HF: HF eq. = Brillouin Theorem $\langle\psi_{HF}\|Hs_i^\dagger\|\psi_{HF}\rangle = 0$ $s_i^\dagger$; single excitation op.	SAC: Generalized Brillouin Theorem $\langle\Psi_g\|(H - E_g)S_I^\dagger\|\Psi_g\rangle = 0$ $S_I^\dagger$; general excitation op.
EXCITED	HF-SECI $\Phi_k = s_k^\dagger\psi_{HF}$ $\langle\Phi_k\|\psi_{HF}\rangle = 0$ $\langle\Phi_k\|H\|\psi_{HF}\rangle = 0$ $\psi_e^{HF\text{-}SECI} = \sum_k d_k\Phi_k$ theoretically consistent only within single excitations	SAC-CI $\Phi_K = P S_K^\dagger\Psi_g$ $\langle\Phi_K\|\Psi_g\rangle = 0$ $\langle\Phi_K\|H\|\Psi_g\rangle = 0$ $\Psi_e^{SAC\text{-}CI} = \sum_K d_K\Phi_K$ theoretically consistent at any stage up to exact limit
	$\Psi_e \simeq$ single Φ_k "frozen-orbital app."	$\Psi_e \simeq$ single Φ_K "frozen-correlation app."

valid for a *general* excitation operator $S_I^\dagger$. In the HF-SECI method, the excited state is described by a linear combination of the singly excited configurations, $\Phi_k = s_k^\dagger\psi_{HF}$ which are orthogonal and Hamiltonian orthogonal to the HF ground state. This relation is just similar to the relation given by Eq. (6) for the SAC-CI theory. In the HF-SECI theory, such a relation is valid only within single excitations, but in the SAC-CI theory it is valid, in principle, at any stage up to an exact limit. As we often approximate an excited state by a single function Φ_k, which is called a frozen-orbital approximation, we may also approximate an excited state by a single function Φ_K. This approximation may be called a "frozen-correlation" approximation. On the other hand, as the HF theory for open-shell and excited states exists [28], the SAC theory is also applicable to open-shell and excited states and some applications have actually been reported [2,10]. Although the calculation is more time consuming than the SAC-CI theory, we may expect more accurate results.

3. Calculation of Ionization and Excitation Spectra of NO Radical

We calculate the closed-shell ground state of the NO cation by the SAC theory and its singlet and triplet excited states by the SAC-CI theory [29]. As for the excited states, we consider not only the singly excited states, as represented by the configurations Φ_1 and Φ_2 in Figure 2, but also the doubly excited states, as represented by Φ_3 in Figure 2. The ground state of the NO radical and its excited states are calculated by the SAC-CI theory as the electron attached states of the NO cation.

The geometry of NO is fixed at the experimental one, $R_{NO} = 1.15\ 077$ Å [30]. The basis set is [5*s*2*p*] CGTOs of Huzinaga–Dunning augmented with *d*-polarization functions on N ($\zeta = 0.80$) and O ($\zeta = 0.85$) and with the Rydberg-type *sp* functions on N ($\zeta_s = 0.028$, $\zeta_p = 0.025$) and O ($\zeta_s = 0.032$, $\zeta_p = 0.028$) [31].

In the actual calculations, we have to introduce several approximations. The calculational scheme was summarized previously [3,5]. For the SAC calculation of the NO cation and the SAC-CI calculation of the NO radical, the thresholds λ_g and λ_e for the selections of the linked operators [5] were 2×10^{-5} and 1×10^{-5} a.u., respectively.* The number of linked operators was 1185 and 1294, respectively. For the singlet and triplet excited states of the NO cation, we carried out two types of calculations. One is an ordinary calculation of reasonable accuracy with a larger number of configurations. The threshold λ_e was 4×10^{-5} a.u. for singlet and 2×10^{-5} a.u. for triplet. The number of linked operators was 2423 for singlet and 2604 for triplet. The other is a smaller size calculation with $\lambda_e = 1 \times 10^{-3}$. The number of linked operators was 1020 for singlet and 1004 for triplet. This smaller size calculation was necessary because we have to solve 300 ~ 400 ionized states in order to study the ionization spectrum in the 10–50 eV range. The matrices were diagonalized by the Hausholder-bisection method [32], keeping matrices in cpu of the computer.

To include an adequate amount of electron correlation, we have to include up to double excitations from the main reference configurations of the states [25]. Since the inner-valence ionized states of the NO radical include both one- and two-electron excited states relative to the ground state of the NO cation, we have to consider up to three- and four-electron excited configurations. In the SAC-CI theory, these terms are included in the unlinked terms and do not affect the dimension of the matrices to be diagonalized. Because of this merit, we can study inner-valence ionizations with relatively small dimensions, in contrast to an ordinary MR-CI method. The linked operators to be included also in the unlinked terms were selected from the magnitudes of their coefficients $|C_I|$ in an ordinary (1 + 2)CI including only linked operators. As for single excitation operators, we have included those whose $|C_I|$ is larger than 0.089. As for double excitation operators, we have included those whose $|C_I|$ in the first 30 solutions are larger than 0.1, or larger than 0.3 in the next 270 solutions. As the double excitation operators $S_I^\dagger$ in the unlinked term which transfer electron correlation from the ground state, we have included those whose coefficients in the ground state (1 + 2)CI are larger than 1×10^{-3}. In the larger size calculations, we have included only up to three-electron excited configurations, since there we have solved only outer-valence singly excited states for which the effect of four-electron excited configurations should be small.

*The values of the thresholds λ_g and λ_e were four times larger for the operators of the types $i = j$ or $a = b$ in $S_i^a S_j^b$ (singlet), $T_i^a S_j^b$ (triplet), $I_i S_j^a$ (ionized), and $A^a S_i^b$ (electron attached).

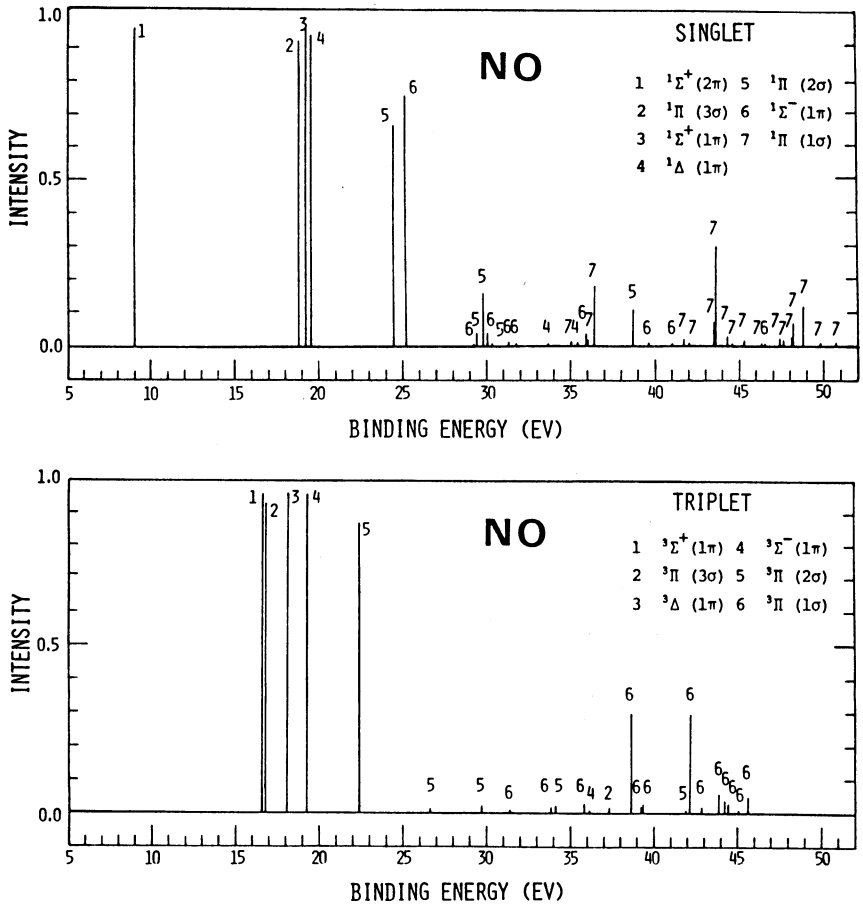


Figure 3. Theoretical ionization spectra of the NO radical calculated by the SAC and SAC-CI theory. Top shows singlet manifold contribution, the bottom triplet manifold contribution. The sum of them are given in Figure 4.

4. Ionization Spectra of NO Radical

Figures 3 and 4 show the theoretical ionization spectra of the NO radical calculated by the present theory. The top of Figure 3 shows the singlet manifold contribution, the bottom the triplet manifold contribution, and Figure 4 shows the sum of them. They are obtained by the smaller size calculations. The energies are relative to the ground state of the NO radical calculated at -129.55479 a.u. Referring to the review due to Grein and Kapur [18], this is the second lowest energy next to the result of Ferguson [33]. In Tables II and III, we have summarized more detailed information of the theoretical peaks for the singlet and triplet manifolds, respectively. The spectral intensity was assumed to be proportional to the transition monopole [34]

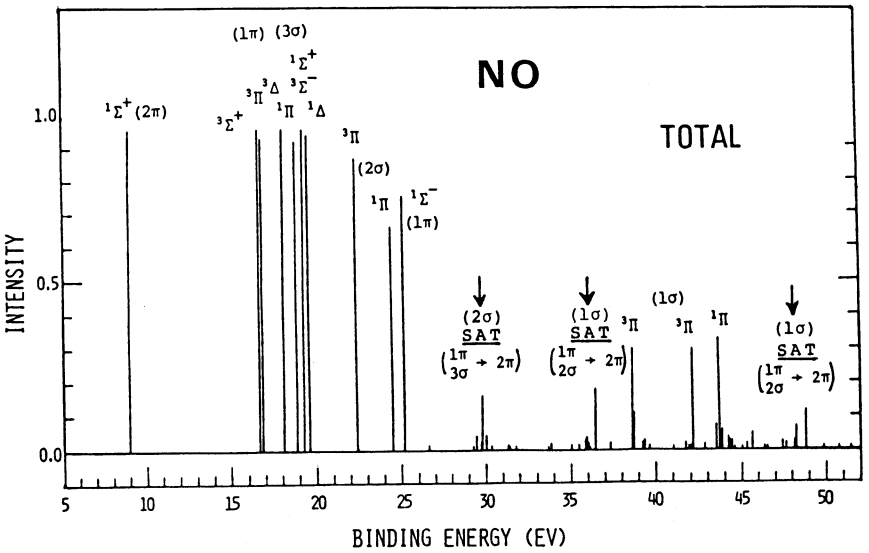


Figure 4. Theoretical ionization spectrum of the NO radical calculated by the SAC and SAC-CI theory. The singlet and triplet contributions are given in Figure 3.

$$P_K = \sum_i |\langle \Psi_K^+ | a_i \Psi_g \rangle|^2$$
$$\simeq \sum_i^{\text{occ}} |\langle \Psi_K^+ | a_i \Phi_0 \rangle|^2$$

where Ψ_K^+ is the Kth ionized state, a_i is an annihilator for an electron in the orbital ϕ_i, and Φ_0 is the Hartree–Fock configuration. The intensity was calculated only for the smaller size calculations. In Tables II and III, we have given the information only for those peaks whose intensities are larger than 0.03, although as Figure 3 shows there were many peaks of weaker intensities.

The theoretical ionization spectrum shown in Figure 4 seems to reproduce well the general features of the experimental spectra shown in Figure 1. In the outer-valence region (8–25 eV), the theoretical peaks give a detailed assignment of the three large peaks observed in the $(e, 2e)$ spectrum and the more resolved peaks in the ESCA spectrum. In Tables II and III, we have compared the present results with those obtained by the high-resolution photoelectron spectroscopy [14]. The peaks lower than 20 eV are due essentially to the single ionization process, as seen from the intensity P. Then, between the smaller and larger size calculations, the latter should be more reliable although it does not include four-electron excited configurations. Actually, the results of the larger size calculation compare well with the experiment. The smaller size calculation tends to over-estimate the ionization energy. We note that the assignment of the observed peaks is different from that of Iwata et al. [14]. From CI calculations, Iwata et

TABLE II. Singlet ionized states of the NO radical calculated by the SAC and SAC-CI theory.[a,b]

Peak No.	State	Ionization energy (eV)[c,d] smaller-size calculation	larger-size calculation	Exptl.	Intensity P	Nature of process	Ionizing orbital	Excitation from NO cation
1	$^1\Sigma^+$	9.0	9.02	9.54[e]	0.96	one	2π	ground
6	$^1\Pi$	18.9	18.40	18.27[e]	0.92	one	3σ	$3\sigma \rightarrow 2\pi$
7	$^1\Sigma^+$	19.3	18.55	18.32[e]	0.95	one	1π	$1\pi \rightarrow 2\pi$
8	$^1\Delta$	19.6	18.96	18.51[e]	0.94	one	1π	$1\pi \rightarrow 2\pi$
10	$^1\Pi$	24.5	24.62	23.3[f]	0.66	one	2σ	$2\sigma \rightarrow 2\pi$
11	$^1\Sigma^-$	25.3	24.81	~ 24[g]	0.76	one	1π	$1\pi \rightarrow 2\pi$
	$^1\Pi$	29.4			0.04	two	2σ	$(1\pi \rightarrow 2\pi, 3\sigma \rightarrow 2\pi)$
	$^1\Pi$	29.8		~ 28[g]	0.16	two	2σ	$(1\pi \rightarrow 2\pi, 3\sigma \rightarrow 2\pi)$
	$^1\Sigma^-$	30.1			0.04	two	1π	$(1\pi \rightarrow 2\pi, 1\pi \rightarrow 2\pi)$
	$^1\Sigma^+$	35.9			0.03	two	1π	$3\sigma \rightarrow 8\sigma$
	$^1\Pi$	36.4		~ 33[g]	0.17	two	1σ	$(1\pi \rightarrow 2\pi, 2\sigma \rightarrow 2\pi)$
	$^1\Pi$	38.7			0.11	two	1σ	$(1\pi \rightarrow 2\pi, 3\sigma \rightarrow 2\pi)$
	$^1\Pi$	43.5			0.07	two	1σ	$1\pi \rightarrow 10\sigma$
	$^1\Pi$	43.7		43.8[f]	0.29	one	1σ	$1\sigma \rightarrow 2\pi$, $(2\sigma \rightarrow 2\pi, 1\pi \rightarrow 2\pi)$
	$^1\Pi$	44.4			0.03	two	1σ	$(1\pi \rightarrow 5\sigma, 1\pi \rightarrow 2\pi)$
	$^1\Pi$	48.2			0.05	two	1σ	$(3\sigma \rightarrow 8\sigma, 3\sigma \rightarrow 2\pi)$
	$^1\Pi$	48.8		~ 47[g]	0.12	two	1σ	$(1\pi \rightarrow 2\pi, 2\sigma \rightarrow 2\pi)$

[a]SAC-CI-V result. The ground state of the NO cation is due to the SAC-NV calculation.

[b]Only the peaks whose intensities are larger than 0.03 are given.

[c]Relative to the ground state of NO radical, -129.55479 a.u., for both smaller size and larger size calculations.

[d]The CI result of Iwata et al. [14] is 9.22 ($^1\Sigma^+$), 17.67 ($^1\Pi$), 18.56 ($^1\Sigma^+$), and 18.97 ($^1\Delta$) in eV.

[e]Ref. 14.

[f]Ref. 11.

[g]Ref. 15.

al. assigned the peaks observed at 18.05 and 18.27 eV to $^1\Pi$ and $^3\Sigma^-$ states, respectively. However, we assign them conversely, i.e., 18.05 eV to $^3\Sigma^-$ and 18.27 eV to $^1\Pi$, on the basis of the larger size calculation. Our assignment is the same as that of Turner et al. [12].

We next compare the experimental and theoretical ionization spectra (Figs. 1 and 4) in the inner-valence region. Again, we see an overall similarity between the experimental and theoretical spectra. A large peak at ca. 40 eV in the ESCA spectrum is considered to be due to a sum of the two peaks of the $^3\Pi$ states

TABLE III. Triplet ionized state of NO radical calculated by the SAC-CI theory.[a]

Peak NO.	State	Ionization energy (eV)[b,c] smaller-size calculation	larger-size calculation	Exptl.	Intensity P	Nature of process	Ionizing orbital	Excitation from NO cation
2	$^3\Sigma^+$	16.7	15.87	16.11[d]	0.96	one	1π	$1\pi \rightarrow 2\pi$
3	$^3\Pi$	16.8	16.35	16.56[d]	0.93	one	3σ	$3\sigma \rightarrow 2\pi$
4	$^3\Delta$	18.1	17.31	17.34[d]	0.96	one	1π	$1\pi \rightarrow 2\pi$
5	$^3\Sigma^-$	19.3	18.25	18.05[d]	0.96	one	1π	$1\pi \rightarrow 2\pi$
9	$^3\Pi$	22.4	21.85	21.7[e]	0.87	one	2σ	$2\sigma \rightarrow 2\pi$
	$^3\Pi$	29.7			0.03	two	2σ	$(3\sigma \rightarrow 2\pi, 1\pi \rightarrow 2\pi)$
	$^3\Pi$	35.8			0.03	two	1σ	$(1\pi \rightarrow 2\pi, 2\sigma \rightarrow 2\pi)$
	$^3\Pi$	38.7		40.6[e]	0.31	two/one	1σ	$(2\sigma \rightarrow 2\pi, 1\pi \rightarrow 2\pi)$
	$^3\Pi$	39.3			0.03	two	1σ	$(1\pi \rightarrow 2\pi, 2\sigma \rightarrow 2\pi)$
	$^3\Pi$	42.2		40.6[e]	0.30	two/one	1σ	$(2\sigma \rightarrow 2\pi, 1\pi \rightarrow 2\pi)$
	$^3\Pi$	43.8			0.06	two	1σ	$(1\pi \rightarrow 3\pi, 3\sigma \rightarrow 2\pi)$
	$^3\Pi$	44.2			0.04	two	1σ	$(3\sigma \rightarrow 4\sigma, 2\sigma \rightarrow 2\pi)$
	$^3\Pi$	45.6			0.05	two	1σ	$(1\pi \rightarrow 4\pi, 3\sigma \rightarrow 2\pi)$

[a]SAC-CI-V result. Only the peaks whose intensities are larger than 0.03 are given.

[b]Relative to the ground state of the NO radical, -129.55479 a.u., for both smaller and larger size calculations.

[c]The CI result of Iwata et al. [14] is 15.65 ($^3\Sigma^+$), 15.87 ($^3\Pi$), 17.25 ($^3\Delta$), and 18.22 ($^3\Sigma^-$) in eV.

[d]Ref. 14.

[e]Ref. 11.

calculated at 38.7 and 42.2 eV. The shoulder at 44 eV in the ESCA spectrum is due to the $^1\Pi$ state calculated at 43.7 eV. This result supports the assignment due originally to Siegbahn et al. [11]. These states are all strong mixtures of the single ionization from the 1σ MO and the simultaneous ionization–excitation from 2σ and 1π MOs to 2π MO. In the $(e, 2e)$ spectrum, two broad peaks centered at ca. 28 and ca. 33 eV are observed. In the ESCA spectrum a peak is observed at ca. 31 eV. In the theoretical spectrum, three groups of weak peaks are obtained at ca. 30 eV, ca. 34 eV, and ca. 36 eV. Among these the two strongest peaks are the singlet peaks at 29.8 and 36.4 eV. Referring to Table II, we then assign the peak observed at 28 eV to a satellite of the singlet ionization from 2σ MO ($^1\Pi$). Its principal nature is a simultaneous ionization–excitation from 3σ and 1π MOs to 2π MO. Similarly, the peak observed at 33 eV is assigned to be a satellite of the singlet ionization from 1σ MO ($^1\Pi$) accompanied by a simultaneous ionization–excitation from 2σ and 1π MOs to 2π MO. Brion and Tan further pointed out an existence of a small peak at ca. 47 eV. Certainly, in the theoretical

spectrum a group of small peaks exists at 48–49 eV. They are singlet peaks and the strongest one is at 48.8 eV. We then assign the peak observed at ca. 47 eV by Brion and Tan to a satellite peak of the singlet ionization from 1σ MO ($^1\Pi$) accompanied by a simultaneous ionization–excitation from 2σ and 1π MOs to 2π MO.

As seen from Figure 3, most of the stronger satellite peaks appear in the singlet manifold. In the triplet manifold the mixing of the shake-up configurations is relatively small except for the two peaks at 38.7 and 42.2 eV, which are shake-up peaks from 2σ and 1π MOs to 2π MO rather than the single ionization peaks from the 1σ MO.

Between the two types of shake-up configurations, Φ_2 and Φ_3, shown in Figure 2, the configurations of type Φ_3 are much more important than type Φ_2 for the NO radical. Among the peaks whose intensities are larger than 0.03, the peaks corresponding to type Φ_2 are only two. Both are in the singlet manifold and at 35.9 and 43.5 eV. They are the shake-up states from 3σ and 2π MOs to 8σ MO and from 1π and 2π MOs to 10σ MO. Both 8σ and 10σ MOs are the valence-type strongly antibonding orbital.

In the theoretical ionization spectrum, we see many peaks of relatively small intensities. This should be a reason for the broadness of the observed peaks in the inner-valence region. Further, all of the shake-up configurations involve the ionization–excitation from bonding or nonbonding MO to antibonding MO. Therefore, the geometry of the shake-up state should differ strongly from that of the ground state. This should also be a reason for the broadness of the spectrum.

5. Excited States of NO Radical

Table IV shows the vertical excitation energy of the NO radical calculated by the SAC-CI theory. They are the excitations from the singly occupied 2π MO to the unoccupied Rydberg orbital. The excitations from occupied MO to the 2π MO were not calculated here. The SAC-CI results are in good agreement with the

TABLE IV. Vertical excitation energy of the NO radical (eV).

State	Orbital picture	Koopmans	SAC-CI[a]	Exptl.[b]	CI[c] Kapur Grein
$A\ ^2\Sigma^+$	$2\pi \rightarrow 3s\sigma$	5.41	5.31	5.45	5.38
$C\ ^2\Pi$	$2\pi \rightarrow 3p\pi$	6.40	6.39	6.46	6.50
$D\ ^2\Sigma^+$	$2\pi \rightarrow 3p\sigma$	6.41	6.40	6.58	6.56
$E\ ^2\Sigma^+$	$2\pi \rightarrow 4s\sigma$	7.58	7.62	7.52	
$H\ ^2\Pi$	$2\pi \rightarrow 3d\pi$	7.80	7.83	7.75	

[a]Relative to the $X\ ^2\Pi$ ground state, -129.55479 a.u.
[b]Ref. 30.
[c]Ref. 18.

experimental values. However, note that even Koopmans relation gives a satisfactory agreement with experiment. This is probably due to a cancellation of the orbital reorganization effect and the difference of the electron correlations between initial and final states.

6. Conclusion

We have studied the ionization spectrum of the NO radical from outer- to inner-valence regions by the SAC and SAC-CI theories. Different from the ionization of closed-shell molecules, the ionization spectrum of the doublet radical is more complex because of the multiplet nature of the ionized states. The theoretical ionization spectrum has reproduced well the general features of the experimental spectrum observed by ESCA and (*e*, 2*e*) spectroscopies. We have given the assignments of all the peaks observed in the outer- and inner-valence regions. For the inner-valence region, this is the first study of the correlation effects in the ionized states of doublet radicals. The origins of the three unassigned peaks observed by the (*e*, 2*e*) spectroscopy are clarified. They are all due to the singlet ionizations. The peak at 28 eV is a satellite of the 2σ ionization. The main origin is the simultaneous ionization–excitation from 1π and 3σ MOs to 2π MO. The second and third peaks at around 33 and 47 eV are both satellites of the 1σ ionization. The main origins of these peaks are the simultaneous ionization–excitation from 2σ and 1π MOs to 2π MO. For the NO radical, the satellite peaks are due mainly to the shake-up configurations of type Φ_3 of Figure 2. The contributions of type Φ_2 were small. Further, most of the stronger satellite peaks appear in the singlet manifold. In the triplet manifold, the intensity of the ionization from 1σ MO is split into two peaks due to a strong interaction with the ionization–excitation configuration from 2σ and 1π MOs to 2π MO. With this exception, the intensities of the satellite peaks were small in the triplet manifold.

In the outer-valence region of the ionization, the present result is in good agreement with the observed spectrum especially when we perform the larger size calculations. The assignments of the ionized states were the same as those given previously by Turner et al. [12]. They were slightly different from those due to the CI calculations by Iwata et al. [14]. The excitation energy of the NO radical was also calculated in good agreement with experiments.

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