

**CLUSTER EXPANSION OF THE WAVEFUNCTION.
SATELLITE PEAKS OF THE INNER-VALENCE IONIZATION OF H₂O
STUDIED BY THE SAC AND SAC CI THEORIES**

Hiroshi NAKATSUJI and Tejiro YONEZAWA

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

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Electron correlation effects on inner-valence ionization and its satellites in water are studied by symmetry-adapted-cluster (SAC) and SAC CI theories. The cluster approximation of electron seems to be adequate even for the shake-up (simultaneous ionization–excitation) process as it is for ordinary excitation, ionization, and electron attachment processes.

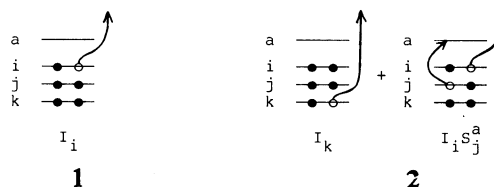
1. Introduction

We are studying systematically the electron correlation in ground and various excited states of molecules by the SAC (symmetry-adapted-cluster) and SAC CI theories [1–7]. So far, this theory has been applied to the ground state of some small molecules and their singlet and triplet excited states, ionized states and electron-attached states, and the results have been encouraging [3–6]. It has also been applied to the spin correlations in open-shell radicals [1,2,7]. In this paper, we apply the theory to the analysis of the satellite peaks of the inner-valence ionization of H₂O [8,9]. We are interested in electron correlation in the shake-up states involved in the satellite peaks because the main configurations are generated from two-electron processes, simultaneous ionization–excitation processes, from the reference Hartree–Fock configuration of the neutral ground state [10–13]. This is in contrast to ordinary excitation, ionization and electron-attachment processes which are essentially one-electron excitations from the Hartree–Fock configuration of the ground state.

2. Electron correlation in the shake-up state

Satellite peaks of inner-valence ionization involve two kinds of correlation effects; initial-state correlation

and final-state correlation [14,15]. The former is calculated here by the SAC expansion method. For the ground state of water, no special correlation effects are involved. On the other hand, the final-state correlation has some interesting complexity. In comparison with an ordinary ionization process, which may be illustrated as **1**, the primary process involved in the satellite peaks is expressed by **2** as a sum of an ionization operator I_k and operators $I_i S_j^a$ which represent simultaneous ionization–excitation (shake-up) processes. This is the reason why one-to-one correspondence between experimental ionization peaks and Hartree–Fock occupied levels is lost. Thus, the origin of the satellite peaks of the inner-valence ionization is essentially electron correlation.



Further, in order to describe accurately the electron correlation of the final state, we have to consider single and double excitations from the correlated main configurations as expressed by **2** in a sense of multi-reference (MR) CI [16]. This leads to a very large number of configurations. A difficulty in the CI ap-

proach lies in that the calculation of satellite peaks requires a solution of many (a few hundred) eigenvalues and eigenvectors of such large hamiltonian matrices. The existing algorithms [17] are difficult to apply for this case. The calculation due to Ågren and Siegbahn [11] is based on semi-internal CI. Kosugi et al. [13] limited their basis set to minimal STO-6G and performed full valence CI. Cederbaum [10] used a quasi-particle formalism based on the Green's function method. Mishra and Öhrn [12] used a more refined formalism, i.e. two-particle-hole Tamm-Dancoff approximation (2ph TDA) [18], based on the Green's function method.

In the SAC CI theory [3], we express the ionized state as

$$\Psi = \sum_K d_K R_K^+ \Psi_g \approx \left[\sum_K d_K R_K^+ + \sum_{KI} d_K C_I R_K^+ S_I^+ \right] |0\rangle, \quad (1)$$

where Ψ_g is the wavefunction of the correlated ground state calculated by the SAC theory, R_K^+ denote one- and two-electron operators of ionization (like I_k and $I_i S_j^a$, respectively, in **2**), and d_K the variational parameters. S_I^+ and C_I are the two-electron excitation operators and their coefficients in the SAC calculation of the ground state and $|0\rangle$ the closed-shell Hartree-Fock reference configuration.

For an ordinary ionization process **1**, the operators R_K^+ in the *unlinked* term, $R_K^+ S_I^+$, can be restricted to only one-electron operators I_i [4]. However, for the shake-up process **2** we have to include both one- and two-electron operators I_k and $I_i S_j^a$ for R_K^+ in the unlinked terms $R_K^+ S_I^+ |0\rangle$. In the SAC CI theory, the operator $\sum_I C_I S_I^+$ applying to $\sum_K d_K R_K^+ |0\rangle$ in the unlinked term represents two-electron excitations from multi-reference configurations in the CI language, the coefficients of the two-electron excitations being transferred from the ground-state calculation. Namely, we express the electron correlation in the excited state, starting from the electron correlation in the ground state.

The present calculations include one- and two-electron excited configurations as linked terms and three- and four-electron excited configurations as unlinked terms. The number of variables in the SAC CI theory is the number of the linked operators only, and the

dimension of the matrices to be diagonalized is greatly reduced in comparison with the MR CI method.

Therefore, though the present method includes a considerable amount of correlation in the ionized states, the matrices to be diagonalized are small enough to be diagonalized by the ordinary QR method, the Householder method, etc. [17]. It is interesting to examine whether the cluster approximation is valid for the two-electron excited states like the shake-up states, as this approximation has already been shown to be good for the one-electron excitation processes like singlet and triplet excitations, outer-valence ionization and electron-attachment processes [3-5].

3. Applications to H₂O

Calculations are carried out for H₂O at the experimental equilibrium geometry (O-H = 1.811 au, \angle HCH = 104.45°). Two kinds of basis sets were used. Basis A is the double-zeta plus polarization functions which are composed of the (4s2p/2s) set of Dunning [19], a set of d functions with the exponent 1.0 on oxygen and a set of p functions with the exponent 0.75 on hydrogen. Basis B is composed of basis A plus two sets of diffuse sp functions on oxygen. The exponents are 0.075172 and 0.023491 for s and 0.053721 and 0.016788 for p [20].

We have adopted a configuration selection scheme [17] as follows to save computer time. For the ground state, double-excitation operators in the linked term were selected by the second-order perturbation energy with the Hartree-Fock configuration larger than 1×10^{-5} au. All of the single-excitation operators were included without selection. In the unlinked term, we have included only such double-excitation operators which have coefficients larger than 5×10^{-3} in the ordinary CI including only the linked terms. For the ionized state, single-excitation (ionization) operators were included without selection and double-excitation operators were selected by the second-order perturbation energy with at least one of the main ionization configurations larger than 1×10^{-5} au. In the unlinked term [see eq. (1)] we have included all single- and double-excitation operators R_K^+ whose coefficients in an ordinary CI are larger than 0.1 and all double-excitation operators S_I^+ whose coefficients in the ground-state CI are larger than 1×10^{-3} . These selection

Table 1
Ground-state correlation energy of water (au)

Method	Previous ^{a)} result	Present result ^{b)}		Ref. [22]	Ref. [23]
		basis A	basis B		
Hartree-Fock	-76.01195	-76.04668	-76.04994	-76.03107	-76.06275
(1 + 2) CI	-0.12840	-0.19375	-0.20574	-0.1575	-0.30559
SAC NV	-0.13422	-0.20081	-0.21304		
SAC V	-0.13285	-0.19933	-0.21134		

a) Ref. [4]. Basis set is (3s2p/2s) + Rydberg sp + anion p [21].

b) Basis A, (4s2p1d/2s1p) set; basis B, basis A + two sets of diffuse sp. See text for details.

criteria were effective for saving computer time without affecting much the final results.

Table 1 shows the ground-state correlation energy calculated by the SAC theory. SAC NV and SAC V show the non-variational and variational solutions, respectively. For the variational solution, some approximations were introduced as reported previously [3]. In the first column, the previous results [4] are cited for comparison. The basis set [21] is similar to basis B but does not include polarization functions for both oxygen and hydrogen. It is seen that the polarization functions are important for the ground state, more important for the correlation energy than for the SCF energy. The unlinked term lowers the correlation energy by ≈ 0.005 – 0.007 au. The CI calculation due to Meyer [23] is very extensive including even f-polarization functions. Buenker and Peyerimhoff [22] have also reported CI calculations for water including the ground and ionized states.

Table 2 shows the valence ionization energy of water. In the SAC CI calculations of the 2B_1 and 2B_2 states, we have included only the one-electron ionization operator I_i for the R_K^+ operators in the unlinked term $R_K^+ S_I^+$ in eq. (1), since these ionizations are essentially one-electron processes in the Hartree-Fock description. For the 2A_1 state, however, we have carried out two kinds of calculation. One is the same level of calculation as for the 2B_1 and 2B_2 states and the other is a calculation for the satellite peaks which includes both one- and two-electron operators for the R_K^+ operators in the unlinked terms. In table 2, the results obtained by the latter method are given in parentheses. It is seen that the effect of the added $R_{(2)} S_{(2)}$ operators is to lower the ionized states. The effect is only ≈ 0.25 eV for the outer-valence ionization ($n \rightarrow \infty$) but

≈ 0.75 eV for inner-valence ionization ($2s \rightarrow \infty$). The effect is larger for the latter than for the former because the mixing of type 2 is larger for the latter (see table 3). In comparison with previous results [4], the present results obtained with basis B compare better with the experimental values. This is mainly due to inclusion of the polarization functions in the present calculation [24]. The result of von Niessen et al. [24] was obtained by the Green's function methods.

Table 3 shows the transition energies, their relative intensities and main configurations for the inner-valence ionization and its satellites of H_2O calculated by the SAC CI method. It also includes the results reported by Ågren and Siegbahn [11]. In the present calculations, relative intensities are assumed to be parallel with the transition monopole [15]

$$P_k = |\langle I_{2a_1} \Psi_g | \Psi_k^+ \rangle|^2,$$

where the operator I_{2a_1} annihilates an electron in the $2a_1$ orbital. Ψ_g and Ψ_k denote the SAC ground state and the k th SAC CI ionized state, respectively. Since the initial-state correlation is not so strong, for H_2O , as the final-state correlation, the relative intensity is very much parallel to the weight of the configuration $I_{2a_1}|0\rangle$ in the SAC CI wavefunction.

Fig. 1 shows the $2a_1$ photoelectron spectrum of water vapour [9]. The bold bars show the present results; the left-hand side shows the result of the SAC CI NV calculation with basis A and the right-hand side shows the result of the SAC CI V calculation with basis B. For comparison the results of Cederbaum [10] and Ågren and Siegbahn [11] are shown on the left-hand side and those of Mishra and Öhrn [12] on the right-hand side.

From fig. 1 it is seen that the position of the main

Table 2
Valence ionization potential of water (eV)

State	Orbital picture	Koopmans' basis B	Δ SCF a)	Ref. [23]	Ref. [22]	Ref. [24]	Present result b)		Exp. [23] a)		
							basis A	basis B			
							SACCIV	SACCIN V	SACCIV	SACCIN V	
$2B_1$	$1b_1(\pi) \rightarrow \infty$	13.86	11.10	12.34	12.13	12.90	11.88	12.28	12.04	12.47	12.61
$2A_1$	$3a_1(n) \rightarrow \infty$	15.87	13.32	14.54	14.06	14.85	14.13 (13.84)	14.53 (14.27)	14.28 (14.07)	14.71 (14.47)	14.73 (14.8 ± 0.1)
$2B_2$	$1b_2(b) \rightarrow \infty$	19.55	17.59	18.73	-	18.91	18.45	18.87	18.58	19.02	18.55 (18.7 ± 0.2)
$2A_1$	$2a_1(2s) \rightarrow \infty$	36.83	34.22	32.25	-	-	32.67 (31.95)	33.08 (32.39)	32.83 (32.12)	33.27 (32.50)	32.19

a) Values in parentheses include vibrational corrections.

b) Values in parentheses are obtained by including the two-electron operators $R(2)$ in the unlinked terms.

Table 3
Inner-valence ionization and its satellite peaks of water

Peak	Ref. [11] a)	This work, basis A, SACCI NV b,c)			This work, basis B, SACCI V d,e)					
		transition energy (eV)	relative intensity	main configuration	transition energy (eV)	relative intensity	main configuration			
1	27.24	6.6	100	0.93 $1b_1^{-2}4a_1^*$	32.39	100	0.84 $2a_1^{-1}$	32.12	100	0.76 $2a_1^{-1}$
2	31.48	100	23	0.82 $2a_1^{-1}$	34.89	23	1.17 $1b_1^{-2}4a_1^*$	34.04	48	0.62 $1b_1^{-2}6a_1^*$
3	32.29	2.5		0.87 $3a_1^{-2}4a_1^*$				36.68	1.1	0.62 $3a_1^{-2}6a_1^*$
4	35.37	16		0.73 $3a_1^{-1}1b_2^{-1}2b_2^*$				39.32	1.3	0.64 $1b_1^{-1}3a_1^{-1}3b_1^*$
5	35.97	14		0.69 $3a_1^{-1}1b_2^{-1}2b_2^*$				40.42	1.4	0.53 $3a_1^{-1}1b_1^{-1}3b_1^*$
6			6.6		40.70	6.6	0.88 $1b_2^{-1}3a_1^{-1}2b_2^*$	40.97	3.5	0.61 $3a_1^{-1}1b_2^{-1}4b_2^*$

a) Transition energy is relative to the ground-state energy, -76.04111 au [11].

b) Transition energy is relative to the ground-state energy, -76.24749 au.

c) The notations $2a_1^{-1}$ and $1b_1^{-1}3a_1^{-1}2b_2^*$ mean the configurations $I_{2a_1}|0\rangle$ and $I_{1b_1}S_{3a_1}^{2b_2}|0\rangle$, respectively.

d) Transition energy is relative to the ground-state energy, -76.26128 au.

e) The results without including the $R(2)S(2)$ operators in the unlinked terms of eq. (1) are as follows. Transition energies (relative intensities) are 32.83 (100), 36.78 (6.0), 39.72 (0.2), 42.33 (0.5), 43.26 (0.8), and 43.82 (1.1) for the peaks 1-6, respectively. Transition energies are in eV and relative intensities in %.

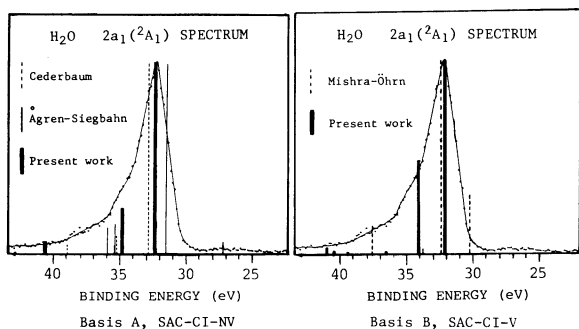


Fig. 1. The $2a_1$ photoelectron spectrum from water vapour [9]. On the left-hand side, the bold bars show the result of the SAC CI NV calculation with basis A, the full bars the result of Ågren and Siegbahn [11], and the dashed bars the result of Cederbaum [10]. On the right-hand side, the bold bars show the result of the SAC CI V calculation with basis B and the dashed bars the result of Mishra and Öhrn [12].

peak is very well reproduced by the present theory. The general feature of the shoulder also seems to be explained. By the calculations with basis A, three peaks are calculated at 32.39, 34.89, and 40.70 eV with relative intensities 100, 23, and 6.6. (The results of the SAC CI V and SAC CI NV were similar, so long as the basis set is the same.) With basis B, these three peaks are calculated at similar positions, 32.12, 34.04, and 40.97 eV with rather different intensities, 100, 48, and 3.5. Further, three weak satellites with intensities less than 2.0 are calculated with basis B between 35 and 41 eV. The shoulders in the energy region higher than the main peak are thus explained.

In the lower-energy region, our calculation did not give satellites stronger than 1.0. Though the $2p-h$ calculation of Mishra and Öhrn and the semi-internal CI calculation of Ågren and Siegbahn gave satellite peaks at 30.2 (intensity 29) and 27.2 eV (intensity 6.6), respectively, these results do not seem to be supported by the experimental spectrum. They are probably due to insufficient inclusion of electron correlation in both the ground and ionized states. (Note that the present basis B is very close to the basis set used by Ågren and Siegbahn.) For example, though the result of Ågren and Siegbahn is relative to the Hartree-Fock ground-state energy -76.04111 au, our result is relative to the correlated ground-state energy -76.26128 au. This shows the difference in the electron correlations included in the ground and ionized states.

Further, it is interesting to note that the assignment

of the main configurations of the satellite peaks of the present work and that of Ågren and Siegbahn (table 3) are different. In our calculation, the main configuration for the strongest satellite at 34.89 (basis A) or 34.04 eV (basis B) is the simultaneous ionization-excitation of the $1b_1(\pi)$ electrons. In the calculation of Ågren and Siegbahn, this is the main configuration of the satellite at 27.24 eV, though the intensity does not seem to agree with the experimental spectrum (fig. 1).

Lastly, we note the importance of the two-electron operators $R_{(2)}$ in the unlinked terms of eq. (1) (i.e. $R_{(2)}S_{(2)}$ operators). In footnote e) to table 3, we have given the transition energies and relative intensities obtained without including the $R_{(2)}S_{(2)}$ operators. Without them, the experimental spectrum shown in fig. 1 cannot be explained. They work to lower the ionized states. The effect is 0.8 eV for the main peak, but 2.7–3.0 eV for the satellite peaks, because the main configuration of the former is essentially a one-electron ionized configuration. Moreover, the relative intensities are also strongly affected. Without the $R_{(2)}S_{(2)}$ operators, the relative intensity of the second peak decreases from 48 to 6. These results show the importance of the $R_{(2)}S_{(2)}$ operators in the unlinked terms of eq. (1) for the description of the satellite peaks.

4. Conclusion

The present study has shown the importance of adequate inclusion of electron correlation in both the ground state and the inner-valence ionization and its satellite states. The present SAC CI theory seems to be a good tool for studying these states. It accounts for the electron correlations of the ionized states through the cluster expansion formalism on the basis of the ground-state correlation [3]. The dimension of the matrix to be diagonalized is much less than that which appears in the ordinary MR CI method, so that we can obtain all of the relevant eigenvalues and eigenvectors necessary for the study of the inner-valence ionization and its satellites.

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