

# Ionization spectra of $XONO_2$ ( $X = F, Cl, Br, I$ ) studied by the SAC–CI method

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## Abstract

Recently observed valence-shell ionization spectra of  $XONO_2$  ( $X = F, Cl, Br, I$ ) are investigated by the SAC–CI (symmetry-adapted-cluster configuration-interaction) method. This is the first attempt to give the quantitative assignments for these molecules by the reliable *ab initio* calculations including electron correlations. Calculated spectra agree very well with the experimental ones, especially for  $FONO_2$  and  $ClONO_2$ . New assignments are proposed for the primary peaks in the outer-valence region, which were characterized by the Koopmans theorem in the previous experimental work. It is also found that there are many shake-up states with considerable intensity in the inner-valence region, especially for  $BrONO_2$  and  $IONO_2$ . The theoretical ionization spectrum of  $IONO_2$  is presented prior to the experimental observations. © 1998 Elsevier Science B.V.

## 1. Introduction

It is well-known that halogen atoms play an important role in the ozone depletion catalytic cycle in the atmosphere. ClO, which appears in the ozone depletion cycle reacts with  $NO_2$  to produce  $ClONO_2$  [1,2], therefore,  $ClONO_2$  is considered to be one of the important temporary reservoir species for Cl atom [3]. In this sense, series of  $XONO_2$  ( $X = F, Cl, Br, I$ ) molecules are important in atmospheric chemistry. Actually,  $XONO_2$  is involved in the chemical reactions in the polar stratospheric clouds for ozone depletion [4–6].

Recently, Wang and his collaborators reported He I photoelectron spectra of  $XONO_2$  ( $X = F, Cl, Br$ ) and investigated the binding energies and the elec-

tronic structures of these molecules [7–9]. They assigned the ionization peaks with help of the Koopmans theorem using *ab initio* MOs and the vibrational structures of the observed peaks. However, there are dense valence states in a very narrow energy region, and therefore reliable theoretical calculations including electron correlations are necessary for the final assignments.

The SAC (symmetry adapted cluster)/SAC–CI method [10–13] has been successfully applied to various kinds of spectroscopies [14,15]. In the applications to the ionization spectra, SAC–CI (SD–R) method, in which the linked ionization operators consists of single and double excitation operators, has reproduced primary peaks in the outer-valence region quite accurately [14–23]. SAC–CI (general-R) method [24–27], in which the linked excitation operators are not limited to singles and doubles but further involve triples and higher ones, was also

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proposed to describe the electron correlations of the multiple excitation processes in high accuracy. The method has been shown to be useful for analyzing the satellite peaks or the shake-up states which are often observed in the inner valence region [28]. In the present study, we use the SAC–CI (SD-R) method for the theoretical assignments of the valence-shell photoelectron spectra of  $XONO_2$  ( $X = F, Cl, Br$  and  $I$ ). We are mainly interested in the characterizations and the interpretations of the primary peaks in the outer-valence region. The SAC–CI(SD-R) method gives quite accurate results for the primary peaks and is extremely efficient.

## 2. Computational details

The ground and ionized states of  $XONO_2$  ( $X = F, Cl, Br, \text{ and } I$ ) are calculated. The basis set is composed of the [5s3p] GTOs of Huginaga and Dunning [29,30] augmented with the polarization  $d$ -functions of  $\zeta_d = 0.8, 0.85, \text{ and } 0.90$  for N, O and F atoms, respectively. For Cl atom, the basis of [6s5p] GTOs with  $d$ -function of  $\zeta_d = 0.514$  is used. For Br and I atoms, relativistic effective core potential [31] is used with [3s2p] plus  $d$ -function of  $\zeta_d = 0.389$  (Br) and 0.266 (I) [32]. The resultant SCF dimensions are 100, 107, 95, and 95 for  $XONO_2$  ( $X = F, Cl, Br, \text{ and } I$ ), respectively. In order to examine the ground state equilibrium geometries of these molecules, HF and MP2 optimizations are performed with the DZP basis sets using Gaussian 92 [33]. Optimized structures are compared with experiment and are adopted for the calculations of vertical ionization potentials (IPs).

Electron correlations of the ground and ionized states are calculated by the SAC/SAC–CI method. In the SAC/SAC–CI calculations, 1s orbitals of O, N, F and 1s, 2s, 2p orbitals of Cl atom are restricted as cores and the counterparts of these MOs are excluded from the active space. Resultant active spaces are  $12 \times 76$  (12 occupied MOs and 76 unoccupied MOs),  $12 \times 75$ ,  $12 \times 71$ , and  $12 \times 71$  for  $XONO_2$  ( $X = F, Cl, Br, \text{ and } I$ ), respectively. In the following discussions and tables, MOs are numbered within the valence orbitals commonly for  $XONO_2$  ( $X = F, Cl, Br, \text{ and } I$ ). In order to reduce the computational effort, configuration selection is performed

Table 1  
Dimensions of the SAC/SAC–CI calculations for  $XONO_2$  ( $X = F, Cl, Br, \text{ and } I$ )

Molecule	Ground state	Ionized state	
		$A'$	$A''$
FONO <sub>2</sub>	14 708	3636	2913
ClONO <sub>2</sub>	14 217	3491	2783
BrONO <sub>2</sub>	13 771	3221	2710
IONO <sub>2</sub>	13 474	3482	2860

in the perturbative way [16,23]. For the ground state, the threshold of the linked term is set to  $\lambda_g = 1 \times 10^{-5}$  and the unlinked terms are adopted as the products of the important linked terms whose SDCl coefficients are larger than 0.001. For ionized state, the threshold of the linked term is set to  $\lambda_e = 1 \times 10^{-5}$ . In the configuration selection for the ionized state, the reference configurations have the coefficients larger than 0.05 in the lowest 30 vectors of the small SDCl for each symmetry. The thresholds for the unlinked terms in the SAC–CI are set to 0.1 and 0.001 for selecting the important  $S$  and  $R$  operators, respectively. The contribution of  $S(2) \times R(2)$  unlinked terms, i.e., so-called ‘3,4-excited’ terms [16] is also included. The dimensions of the SAC/SAC–CI calculations are summarized in Table 1. The HF SCF orbitals are obtained by HONDO8 program [34] and the SAC–CI calculations are performed by the SAC–CI96 program system [35].

## 3. Results and discussions

### 3.1. Equilibrium geometry of $XONO_2$

The ground state equilibrium geometries of  $XONO_2$  ( $X = F, Cl, \text{ and } Br$ ) have been extensively studied in many theoretical and experimental works [36–41]. It is now commonly recognized that these molecules have planar structures. Recently, detailed structures of these molecules were re-examined by the electron diffraction experiment [36,37]. It was also pointed out that the theoretically optimized geometry of FONO<sub>2</sub>, especially the N–O bond length, is very dependent on the level of calculations [37]. Such problems also occur in other molecules including electro-negative atoms like FOOF and FONO.

Table 2

Equilibrium structures of  $XONO_2$  ( $X = F, Cl, Br, \text{ and } I$ ) calculated by the HF and MP2 method with DZP basis sets

	FONO <sub>2</sub>			ClONO <sub>2</sub>			BrONO <sub>2</sub>			IONO <sub>2</sub>	
	HF	MP2	Exptl. <sup>a</sup>	HF	MP2	Exptl. <sup>b</sup>	HF	MP2	Exptl. <sup>b</sup>	HF	MP2
$r_{XO}$	1.343	1.434	1.409	1.675	1.703	1.673	1.817	1.863	1.829	1.986	2.028
$r_{ON}$	1.386	1.559	1.507	1.372	1.548	1.499	1.359	1.518	1.456	1.344	1.476
$r_{NO_c}$	1.171	1.200	1.184	1.178	1.204	1.196	1.182	1.214	1.205	1.188	1.205
$r_{NO_t}$	1.176	1.212	1.184	1.178	1.207	1.196	1.179	1.217	1.205	1.180	1.205
$\angle XON$	108.6	105.2	106.0	115.8	111.2	113.0	117.6	113.0	113.9	119.9	115.2
$\angle ONO_t$	109.8	107.6	108.4	111.0	107.7	108.8	111.9	108.3	106.6	113.2	109.7
$\angle ONO_c$	118.2	116.3	117.1	118.6	117.3	118.6	118.6	118.0	119.5	118.2	119.5

<sup>a</sup> Ref. [36].<sup>b</sup> Ref. [37].

Since it is very important to use correct molecular geometries in order to obtain accurate vertical ionization spectra, we have examined the geometry opti-

mizations using several different basis sets for  $XONO_2$  ( $X = F, Cl, Br, \text{ and } I$ ). In particular, a reliable geometry of  $IONO_2$  is not available [42].

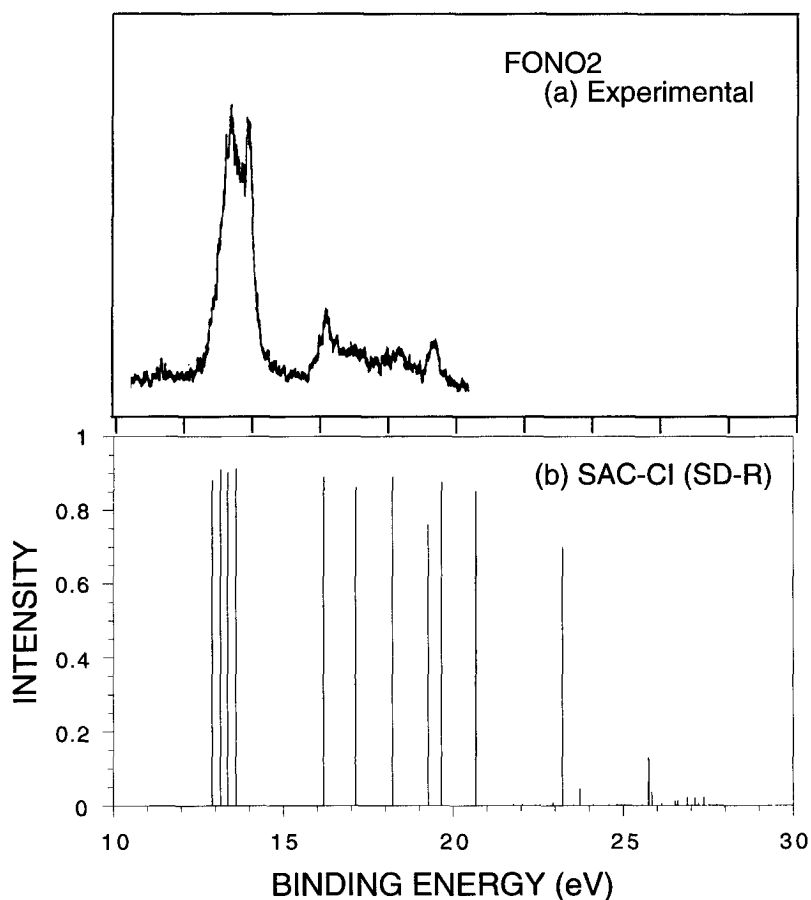


Fig. 1. (a) Experimental and (b) SAC-CI ionization spectra of FONO<sub>2</sub>. Experimental photoelectron spectrum is cited from Ref. [7].

In Table 2, we give the representative results; namely the HF and MP2 optimized geometries due to the DZP basis sets. In general, MP2 optimization gives more reliable results than with HF. It is found that an addition of the polarization function reduces the bond lengths of OX and NO and an inclusion of electron correlations has opposite effect. The HF geometry optimization gives NO bond lengths being too small (0.102–0.121 Å) and this causes a critical problem for the calculations of ionization potentials. The MP2 optimization overestimates the OX bond length by 0.025–0.034 Å and the NO bond length by 0.038–0.052 Å. Bond angles estimated by MP2 are fairly good, the errors are within 2° for all molecules. In this way, we confirm that the above-mentioned problem also happens in all the XONO<sub>2</sub> species. The geometries obtained by the MP2 optimization

with the DZP basis sets agree well with the results of the CCSD(T)/TZ2P calculations by Lee [38]. We therefore, adopt these geometries throughout the present study.

### 3.2. FONO<sub>2</sub>

The experimental [7] and SAC–CI theoretical ionization spectra of FONO<sub>2</sub> are compared in Fig. 1. Photoelectron spectrum was recorded up to 20 eV, while the inner-valence region is also examined in the present study. In Table 3, calculated IPs, monopole intensities, and characters are given for both the primary states and some low-lying shake-up states.

In the experimental spectrum, two vibrational progressions are observed in the first peak at 13.21 eV.

Table 3

Ionization potential (in eV), monopole intensity, and ionization character of FONO<sub>2</sub> (MOs are numbered within the valence orbitals)

	Koopmans	Exptl. <sup>a</sup>	SAC–CI		
			IP	Intensity <sup>b</sup>	Ionization character <sup>c</sup>
<sup>2</sup> A''	14.52	13.21	12.91	0.88	(4a'') <sup>-1</sup> π(n, O <sub>2</sub> (N)) <sup>-1</sup>
<sup>2</sup> A'	15.08		13.16	0.91	(11a') <sup>-1</sup> σ(n, O <sub>2</sub> (N)OF) <sup>-1</sup>
<sup>2</sup> A'	15.67	13.65	13.36	0.90	(10a') <sup>-1</sup> σ(n, O <sub>2</sub> (N)) <sup>-1</sup>
<sup>2</sup> A''	16.21		13.60	0.91	(3a'') <sup>-1</sup> π(a, OF) <sup>-1</sup>
<sup>2</sup> A'	18.74	16.24	16.19	0.89	(9a') <sup>-1</sup> σ(n, FON) <sup>-1</sup>
<sup>2</sup> A''	20.45	17.05	17.13	0.86	(2a'') <sup>-1</sup> π(b, FONO <sub>2</sub> ) <sup>-1</sup>
<sup>2</sup> A'	20.04	18.19	18.21	0.89	(8a') <sup>-1</sup> σ(b, OF) <sup>-1</sup>
<sup>2</sup> A''	22.28	19.17	19.26	0.76	(1a'') <sup>-1</sup> π(b, NO <sub>2</sub> OF) <sup>-1</sup>
<sup>2</sup> A'	22.00		19.66	0.88	(7a') <sup>-1</sup> σ(b, NO <sub>2</sub> ) <sup>-1</sup>
<sup>2</sup> A'	23.27		20.67	0.85	(6a') <sup>-1</sup> σ(b, NO <sub>2</sub> OF) <sup>-1</sup>
<sup>2</sup> A'			22.93	0.007	
<sup>2</sup> A'	26.22		23.22	0.700	(5a') <sup>-1</sup> σ(n, NO <sub>2</sub> OF) <sup>-1</sup>
<sup>2</sup> A'			23.74	0.045	
<sup>2</sup> A'			25.75	0.062	
<sup>2</sup> A''			25.76	0.125	
<sup>2</sup> A'			25.85	0.036	
<sup>2</sup> A'			26.14	0.006	
<sup>2</sup> A'			26.53	0.013	
<sup>2</sup> A''			26.61	0.013	
<sup>2</sup> A'			26.89	0.022	
<sup>2</sup> A''			27.12	0.019	
<sup>2</sup> A'			27.38	0.022	

<sup>a</sup> Ref. [7].

<sup>b</sup> Ionized states whose intensity is larger than 0.005 are shown.

<sup>c</sup> a, b, and n denote anti-bonding, bonding, and non-bonding MOs, respectively.

In the present calculation, two electronic states,  $(4a'')^{-1}$  and  $(11a')^{-1}$  states, are calculated at 12.91 and 13.16 eV, respectively, and we assign these two states to the first peak. These states are characterized as the ionizations from the orbitals localized on the  $\text{NO}_2$  unit. This is characteristic to  $\text{FONO}_2$  and different from other  $\text{XONO}_2$  molecules as seen below. Next, two ionized states are calculated at 13.36 and 13.60 eV. These closely located states are assigned to the second peak at 13.65 eV. No vibrational structures were observed in this peak. This is partly because one of the state,  $(3a'')^{-1}$  is the ionization from the anti-bonding  $\pi$  orbital localized on OF.

This assignment is different from that of ref. [7], and consequently the assignments for the following states are different.

In the higher energy region, 14–20 eV, a broad band composed of several electronic states is observed but the intensity is rather small because they are the ionizations from the fluorine-dominant MOs [43]. We assign four primary states,  $(9a'')^{-1}$ ,  $(2a'')^{-1}$ ,  $(8a')^{-1}$  and  $(1a'')^{-1}$  to this band. These states are calculated at 16.19, 17.13, 18.21 and 19.26 eV in good agreement with the experimental values 16.24, 17.05, 18.19, and 19.17 eV, respectively. It should be noted that the ordering of these states calculated

Table 4

Ionization potential (in eV), monopole intensity, and ionization character of  $\text{ClONO}_2$  (MOs are numbered within the valence orbitals)

	Koopmans	Exptl. <sup>a</sup>	SAC-CI		
			IP	Intensity <sup>b</sup>	Ionization character <sup>c</sup>
${}^2A''$	13.12	11.56	11.46	0.91	$(4a'')^{-1}$ $\pi(a, \text{ClO})^{-1}$
${}^2A'$	13.45	12.14	12.04	0.92	$(11a')^{-1}$ $\sigma(n, \text{Cl}(\text{NO}))^{-1}$
${}^2A''$	14.22	12.94	12.89	0.91	$(3a'')^{-1}$ $\pi(n, \text{O}_2(\text{N}))^{-1}$
${}^2A'$	15.06		13.15	0.91	$(10a')^{-1}$ $\sigma(n, \text{O}_2(\text{N})\text{OCl})^{-1}$
${}^2A'$	15.47	13.87	13.73	0.91	$(9a')^{-1}$ $\sigma(n, \text{O}_2(\text{N})\text{OCl})^{-1}$
${}^2A''$	17.56	14.68	14.85	0.88	$(2a'')^{-1}$ $\pi(b, \text{OCl}(\text{NO}_2))^{-1}$
${}^2A'$	17.81	16.10	16.20	0.90	$(8a')^{-1}$ $\sigma(b, \text{OCl})^{-1}$
${}^2A''$	21.69	18.78	18.88	0.75	$(1a'')^{-1}$ $\pi(b, \text{NO}_2\text{O})^{-1}$
${}^2A'$			19.14	0.002	
${}^2A'$	21.59		19.29	0.88	$(7a')^{-1}$ $\sigma(b, \text{NO}_2)^{-1}$
${}^2A'$	22.54		20.04	0.84	$(6a')^{-1}$ $\sigma(b, \text{NO}_2\text{OCl})^{-1}$
${}^2A''$			20.69	0.008	
${}^2A'$			20.85	0.009	
${}^2A'$			21.86	0.007	
${}^2A'$			22.31	0.029	
${}^2A'$			22.43	0.034	
${}^2A'$			22.49	0.041	
${}^2A'$	25.47		22.63	0.604	$(5a')^{-1}$ $\sigma(n, \text{NO}_2\text{OCl})^{-1}$
${}^2A'$			22.68	0.005	
${}^2A'$			23.14	0.019	
${}^2A'$			23.53	0.008	
${}^2A'$			23.55	0.041	
${}^2A'$			23.93	0.031	
${}^2A'$			24.64	0.008	
${}^2A''$			24.98	0.014	
${}^2A''$			25.02	0.033	
${}^2A''$			25.17	0.036	
${}^2A'$			25.30	0.020	

<sup>a</sup> Ref. [8].

<sup>b</sup> Ionized states whose intensity is larger than 0.005 are shown.

<sup>c</sup> a, b, and n denote anti-bonding, bonding, and non-bonding MOs, respectively.

by the SAC–CI method is different from that by the Koopmans theorem. Just above the  $(1a')^{-1}$  state, there are two primary states calculated at 19.66 and 20.67 eV which are characterized as  $(7a')^{-1}$  and  $(6a')^{-1}$  states. These states contribute to the edge of the broad band, though, more detailed experimental information is necessary for the final assignment. In addition, a primary state,  $(5a')^{-1}$  is calculated at 23.22 eV, though the intensity is small through the interactions with other shake-up states.

The agreement between theory and experiment is excellent for this molecule and the deviations from

the experimental values are within 0.1 eV. The present theoretical result will also help a future assignment in the inner-valence region of the experimental spectrum.

### 3.3. $\text{ClONO}_2$

Table 4 presents the theoretical assignments of the ionization spectrum of  $\text{ClONO}_2$  and gives the calculated IPs and intensities. Fig. 2 compares (a) the experimental photoelectron spectrum of  $\text{ClONO}_2$  [8] and (b) the SAC–CI theoretical spectrum. The peaks

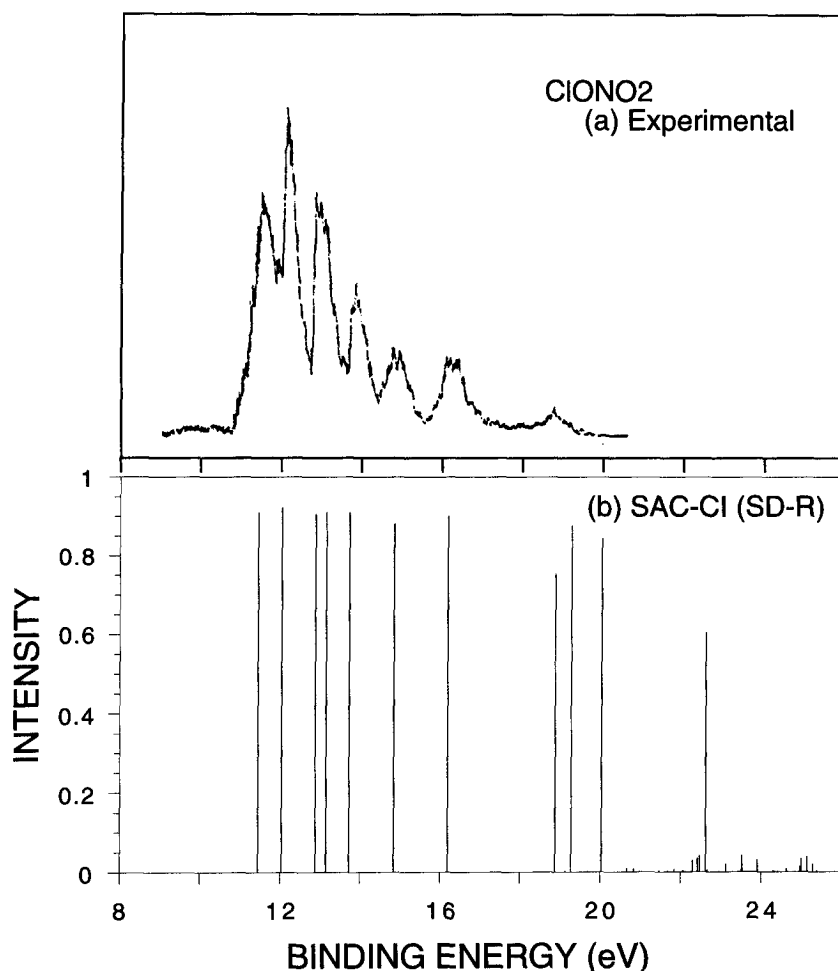


Fig. 2. (a) Experimental and (b) SAC–CI ionization spectra of  $\text{ClONO}_2$ . Experimental photoelectron spectrum is cited from Ref. [8].

are located separately and continuously in this case in comparison with  $\text{FONO}_2$ . This is because the orbital energies of the ClO unit lie very closely to those of the  $\text{NO}_2$  unit.

In the case of  $\text{ClONO}_2$ , the first and second ionized states are well resolved and observed at 11.56 and 12.14 eV above the ground state. These states are assigned to  $(4a'')^{-1}$  and  $(11a')^{-1}$  states calculated at 11.45 and 12.04 eV, respectively, and both are characterized as the ionizations from the orbitals localized on the OCl unit, which is different from the case of  $\text{FONO}_2$ . The third band observed at

12.94 eV was reported to be an overlapping band since different two vibrational structures were observed. In the present calculation, two ionized states,  $(3a'')^{-1}$  and  $(10a')^{-1}$  states, are calculated at 12.89 and 13.15 eV, respectively, and are assigned to this band. This assignment is identical to that of the experimental work [8]. Two vibrational structures of this band are due to the different characters of these two electronic states.

Next three primary peaks observed at 13.87, 14.68, and 16.10 eV are found to be due to the  $(9a')^{-1}$ ,  $(2a'')^{-1}$ ,  $(8a')^{-1}$  states which are calculated at 13.73,

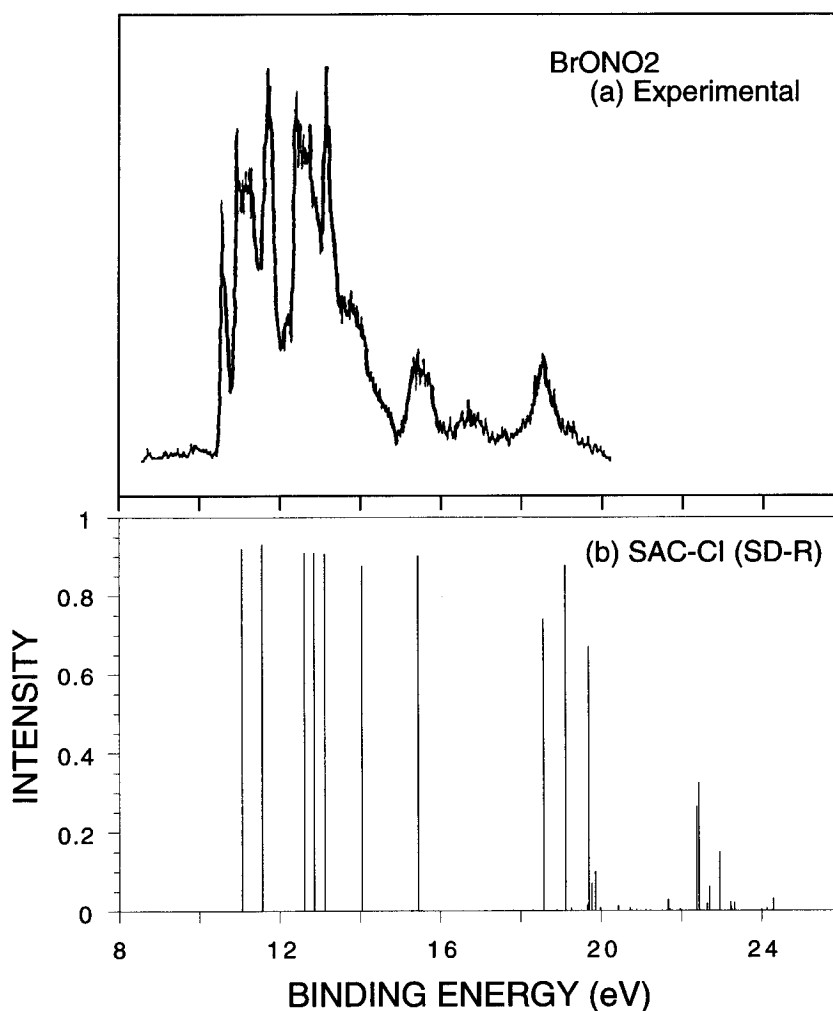


Fig. 3. (a) Experimental and (b) SAC-CI ionization spectra of  $\text{BrONO}_2$ . Experimental photoelectron spectrum is cited from Ref. [9].

14.85, and 16.20 eV, respectively. These three states individually contribute to the three peaks: This assignment is different from that of the Ref. [8]. Around the peak observed at 18.78 eV, two primary states are calculated at 18.88 and 19.29 eV and a shake-up state at 19.14 eV. We assign these primary states,  $(1a'')^{-1}$  and  $(7a')^{-1}$  states, to this peak. The experimental cross section for this peak is too small to further examine this assignment. Other primary states,  $(6a')^{-1}$  and  $(5a')^{-1}$ , are also calculated at 20.04 and 22.63 eV, while the experimental information is missing in this energy region. It should be noted that several shake-up states appear in the

inner-valence region (Table 4), though their intensities are small. Again, the calculated ionization spectrum agrees very well with the experimental one.

### 3.4. $BrONO_2$

Next, we discuss about the ionization spectrum of  $BrONO_2$ . The photoelectron spectrum [9] and the SAC–CI ionization spectrum of  $BrONO_2$  are presented in Fig. 3. Table 5 gives the detailed numerical data in the same way as the previous one.

Split sharp peaks are observed at 10.60 and 10.91 eV. This splitting is explained by the SO interaction

Table 5

Ionization potential (in eV), monopole intensity, and ionization character of  $BrONO_2$  (MOs are numbered within the valence orbitals)

	Koopmans	Exptl. <sup>a</sup>	SAC–CI		
			IP	Intensity <sup>b</sup>	Ionization character <sup>c</sup>
${}^2A''$	12.25	10.60 10.91	11.07	0.92	$(4a'')^{-1}$ $\pi(a, BrO)^{-1}$
${}^2A'$	12.53	11.25	11.57	0.93	$(11a')^{-1}$ $\sigma(n, Br)^{-1}$
${}^2A'$	13.90	11.78	12.61	0.91	$(10a')^{-1}$ $\sigma(n, O_2(N)O(Br))^{-1}$
${}^2A''$	14.76	12.50	12.86	0.91	$(3a'')^{-1}$ $\pi(n, O_2(N))^{-1}$
${}^2A'$	14.90	13.12	13.12	0.91	$(9a')^{-1}$ $\sigma(n, O_2(N)OBr)^{-1}$
${}^2A''$	16.79	13.66	14.04	0.88	$(2a'')^{-1}$ $\pi(b, OBrNO_2)^{-1}$
${}^2A'$	17.07	≈ 15.5	15.45	0.91	$(8a')^{-1}$ $\sigma(b, OBr)^{-1}$
${}^2A'$		≈ 17.0	17.82	0.002	
${}^2A''$	21.35	≈ 18.5	18.57	0.74	$(1a'')^{-1}$ $\pi(b, NO_2O)^{-1}$
${}^2A'$	21.28		19.12	0.88	$(7a')^{-1}$ $\sigma(b, NO_2)^{-1}$
${}^2A'$			19.26	0.007	
${}^2A''$			19.66	0.016	
${}^2A'$	22.11		19.70	0.67	$(6a')^{-1}$ $\sigma(b, NO_2OBr)^{-1}$
${}^2A'$			19.77	0.069	
${}^2A'$			19.86	0.099	
${}^2A''$			19.99	0.007	
${}^2A'$			20.42	0.010	
${}^2A'$			20.43	0.014	
${}^2A'$			20.72	0.007	
${}^2A'$			21.67	0.028	
${}^2A'$			22.39	0.264	
${}^2A'$	25.09		22.44	0.323	$(5a')^{-1}$ $\sigma(n, BrONO_2)^{-1}$
${}^2A'$			22.64	0.019	
${}^2A'$			22.70	0.062	
${}^2A'$			22.95	0.148	
${}^2A'$			23.23	0.022	
${}^2A'$			23.24	0.009	
${}^2A'$			23.33	0.020	
${}^2A''$			24.29	0.029	

<sup>a</sup> Ref. [9].

<sup>b</sup> Ionized states whose intensity is larger than 0.005 are shown.

<sup>c</sup> a, b, and n denote anti-bonding, bonding, and non-bonding MOs, respectively.



in the experimental work on the basis of the analogy to alkyl bromides [43]. In the present study,  $(4a'')^{-1}$  state calculated at 11.07 eV is attributed to these peaks and is characterized as the ionization from the  $\pi$  orbital dominated by the Br atom. Next peak observed at 11.25 eV is assigned to  $(11a')^{-1}$  state calculated at 11.57 eV. There are no suitable candidates for the peak at 11.78 eV. We tentatively attribute  $(15a')^{-1}$  state to this peak. Closely located state observed at 12.50 eV is assigned to  $(3a'')^{-1}$  state calculated at 12.86 eV. The following two peaks observed at 13.12 and 13.66 eV are attributed to  $(9a')^{-1}$  and  $(2a'')^{-1}$  states, which are calculated at 13.12 and 14.04 eV, respectively.

There were no arguments for the peaks above 14 eV in the experimental work [9]. In our calculation, two primary states,  $(8a')^{-1}$  and  $(1a'')^{-1}$ , are calculated at 15.45 and 18.57 eV. These states correspond to the peaks around 15.5 and 18.5 eV in the experimental spectrum. There is a weak broad band around 17 eV and this band is attributed to the shake-up state calculated at 17.82 eV, though the calculated intensity is rather small. In the inner-valence region, the breakdown of the Koopmans picture is remarkable. Theoretical spectrum in this region may be improved by the application of the SAC-CI (general-R) method. Many shake-up states are calculated

around 20–25 eV and detailed experimental study is necessary.

### 3.5. $\text{IONO}_2$

Finally, we present the theoretical ionization spectrum of  $\text{IONO}_2$ . There is no experimental information for this molecule. The theoretical spectrum is shown in Fig. 4 and the numerical data are collected in Table 6.

The first ionized state is  $(4a'')^{-1}$  state and is characterized as the ionization from the  $\pi$  orbital localized on the I atom. Large spin-orbit splitting is therefore expected for this state like in  $\text{BrONO}_2$ . The spin-orbit effect is also expected to be large for  $(11a)^{-1}$  state, since the MO is localized on the iodine. The outer-valence ionization spectrum of  $\text{IONO}_2$  is very similar to that of  $\text{BrONO}_2$ , since the ionizations from the MOs localized on the OX unit are well separated energetically from those on the  $\text{NO}_2$  unit in both molecules. In the inner-valence region, the shake-up states are remarkable in the energy range of 18–20 eV. The intensities of the  $(1a'')^{-1}$ ,  $(6a)^{-1}$  and  $(5a)^{-1}$  single-hole configurations are distributed to these shake-up states.

The spin-orbit interaction should be included for obtaining the detailed ionization spectrum of  $\text{IONO}_2$  and the spectrum in the inner-valence region may be

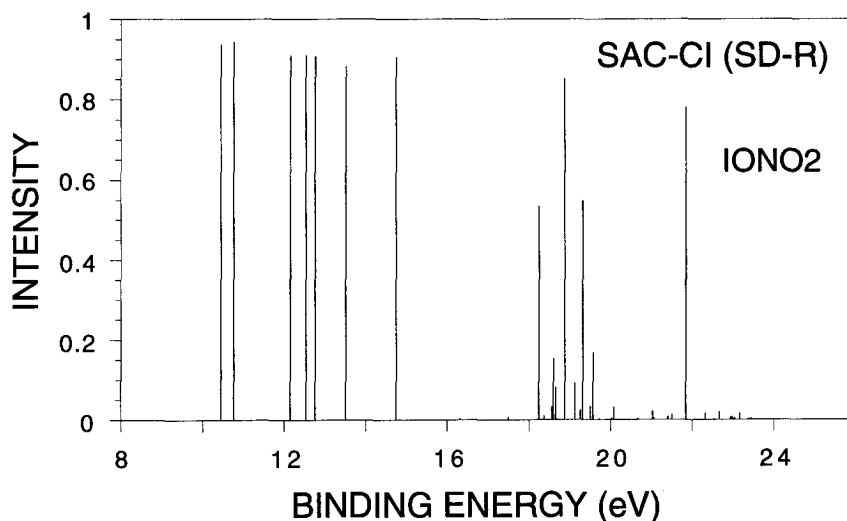


Fig. 4. SAC-CI theoretical ionization spectrum of  $\text{IONO}_2$ .

Table 6

Ionization potential (in eV), monopole intensity, and ionization character of IONO<sub>2</sub> (MOs are numbered within the valence orbitals)

	Koopmans	SAC-CI		Ionization character <sup>b</sup>	
		IP	Intensity <sup>a</sup>		
<sup>2</sup> A''	11.21	10.45	0.94	(4a'') <sup>-1</sup>	π(a, IO) <sup>-1</sup>
<sup>2</sup> A'	11.39	10.76	0.94	(11a') <sup>-1</sup>	σ(n, I) <sup>-1</sup>
<sup>2</sup> A'	14.37	12.15	0.91	(10a') <sup>-1</sup>	σ(n, O <sub>2</sub> (N)OI) <sup>-1</sup>
<sup>2</sup> A''	13.59	12.53	0.91	(3a'') <sup>-1</sup>	π(n, O <sub>2</sub> (N)) <sup>-1</sup>
<sup>2</sup> A'	14.64	12.75	0.91	(9a') <sup>-1</sup>	σ(n, O <sub>2</sub> (N)OI) <sup>-1</sup>
<sup>2</sup> A''	16.14	13.51	0.88	(2a'') <sup>-1</sup>	π(b, OI(N)O <sub>2</sub> ) <sup>-1</sup>
<sup>2</sup> A'	16.51	14.75	0.90	(8a') <sup>-1</sup>	σ(b, OI(N)O <sub>2</sub> ) <sup>-1</sup>
<sup>2</sup> A''		17.50	0.006		
<sup>2</sup> A''	21.10	18.24	0.534	(1a'') <sup>-1</sup>	π(b, NO <sub>2</sub> O) <sup>-1</sup>
<sup>2</sup> A''		18.37	0.010		
<sup>2</sup> A'		18.56	0.032		
<sup>2</sup> A''		18.60	0.151		
<sup>2</sup> A'		18.65	0.012		
<sup>2</sup> A''		18.66	0.080		
<sup>2</sup> A'	20.98	18.87	0.852	(7a') <sup>-1</sup>	σ(b, NO <sub>2</sub> ) <sup>-1</sup>
<sup>2</sup> A'		19.13	0.091		
<sup>2</sup> A'		19.27	0.024		
<sup>2</sup> A'	21.70	19.32	0.548	(6a') <sup>-1</sup>	σ(b, IONO <sub>2</sub> ) <sup>-1</sup>
<sup>2</sup> A'		19.51	0.034		
<sup>2</sup> A'		19.57	0.168		
<sup>2</sup> A'		20.09	0.031		
<sup>2</sup> A'		21.04	0.021		
<sup>2</sup> A'		21.41	0.008		
<sup>2</sup> A'		21.51	0.013		
<sup>2</sup> A'	24.06	21.85	0.780	(5a') <sup>-1</sup>	σ(n, IONO <sub>2</sub> ) <sup>-1</sup>
<sup>2</sup> A''		22.32	0.016		
<sup>2</sup> A'		22.67	0.019		
<sup>2</sup> A''		22.94	0.006		
<sup>2</sup> A'		23.16	0.016		

<sup>a</sup> Ionized states whose intensity is larger than 0.005 are shown.

<sup>b</sup> a, b, and n denote anti-bonding, bonding, and non-bonding MOs, respectively.

improved by the application of SAC-CI(general-R) method. However, the present results should be qualitatively predictive and therefore, should help the assignment of the experimental spectrum in the future.

#### 4. Conclusion

We have investigated the valence-shell ionization spectra of XONO<sub>2</sub> (X = F, Cl, Br, and I) by the SAC-CI (SD-R) method. This is the first quantitative assignments of the ionization spectra of these

molecules by the method including electron correlations. The SAC-CI theoretical spectra reproduces the main peaks of the experimental spectra in high accuracy, especially for FONO<sub>2</sub> and ClONO<sub>2</sub>. Detail characterizations of the ionized states are performed and many new assignments are proposed for the primary peaks in the low-energy outer-valence region. It is also found that there are many shake-up states in the outer- and inner-valence region. In the case of BrONO<sub>2</sub> and IONO<sub>2</sub>, considerable intensities are distributed to these states. Theoretical ionization spectrum of IONO<sub>2</sub> are presented prior to the experimental observation. More detailed analysis of the satellite peaks by the SAC-CI (general-R) method and the calculations including the spin-orbit interaction for BrONO<sub>2</sub> and IONO<sub>2</sub> are now in progress.

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#### References

- [1] F.S. Rowland, J.E. Spencer, M.J. Molina, *J. Phys. Chem.* 80 (1976) 2711.
- [2] F.S. Rowland, J.E. Spencer, M.J. Molina, *J. Phys. Chem.* 80 (1976) 2713.
- [3] F.S. Rowland, *Ann. Rev. Phys. Chem.* 42 (1991) 731.
- [4] M.J. Prather, *Nature* 355 (1992) 534.
- [5] D.R. Hanson, A.R. Ravishankara, *J. Phys. Chem.* 96 (1992) 7674.
- [6] J.P.D. Abbatt, M.J.J. Molina, *J. Phys. Chem.* 96 (1992) 7679.
- [7] D. Wang, Y. Li, P. Jiang, X. Wang, B. Chen, *Chem. Phys. Lett.* 262 (1996) 771.
- [8] D. Wang, Y. Li, P. Jiang, X. Wang, B. Chen, *Chem. Phys. Lett.* 260 (1996) 99.
- [9] D. Wang, J. Peng, *J. Phys. Chem.* 100 (1996) 4382.
- [10] H. Nakatsuji, K. Hirao, *J. Chem. Phys.* 68 (1978) 2053.
- [11] H. Nakatsuji, *Chem. Phys. Lett.* 59 (1978) 362.
- [12] H. Nakatsuji, *Chem. Phys. Lett.* 67 (1979) 329.
- [13] H. Nakatsuji, *Chem. Phys. Lett.* 67 (1979) 334.
- [14] H. Nakatsuji, in: *Computational Chemistry-Review of Current Trends*, Vol. 2, pp. 62–124.
- [15] H. Nakatsuji, *Acta Chim. Hungarica* 129 (1992) 719.

- [16] H. Nakatsuji, *Chem. Phys.* 75 (1983) 425.
- [17] H. Nakatsuji, *Chem. Phys.* 76 (1983) 283.
- [18] H. Nakatsuji, *J. Chem. Phys.* 80 (1984) 3703.
- [19] H. Nakatsuji, O. Kitao, T. Yonezawa, *J. Chem. Phys.* 83 (1985) 723.
- [20] H. Nakatsuji, S. Saito, *J. Chem. Phys.* 91 (1989) 6205.
- [21] H. Nakatsuji, M. Ehara, M.H. Palmer, M.F. Guest, *J. Chem. Phys.* 97 (1992) 2561.
- [22] H. Nakatsuji, M. Ehara, *J. Chem. Phys.* 101 (1994) 7658.
- [23] H. Nakatsuji, J. Hasegawa, M. Hada, *J. Chem. Phys.* 104 (1996) 2321.
- [24] H. Nakatsuji, *Chem. Phys. Lett.* 177 (1991) 331.
- [25] H. Nakatsuji, *J. Chem. Phys.* 83 (1985) 731.
- [26] H. Nakatsuji, *J. Chem. Phys.* 83 (1985) 5743.
- [27] H. Nakatsuji, *J. Chem. Phys.* 94 (1991) 6716.
- [28] M. Ehara, H. Nakatsuji, *Chem. Phys. Lett.*, in press.
- [29] S. Huzinaga, *J. Chem. Phys.* 42 (1965) 1293.
- [30] T.H. Dunning Jr., *J. Chem. Phys.* 53 (1970) 2823.
- [31] P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 299.
- [32] S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, H. Tatewaki, *Gaussian Basis Sets for Molecular Calculations*, Elsevier, Amsterdam, 1984.
- [33] M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. Defrees, J. Baker, J.J.P. Stewart, J.A. Pople, *GAUSSIAN 92*, Gaussian Inc., Pittsburgh, PA, 1992.
- [34] M. Dupuis, A. Farazdel, program system HONDO8, A. MOTECC-91, Center for Scientific and Engineering Computations, IBM Corporation, 1991.
- [35] H. Nakatsuji, M. Hada, M. Ehara, J. Hasegawa, T. Nakajima, H. Nakai, O. Kitao, K. Toyota, SAC/SAC-CI program system (SAC-CI96) for calculating ground, excited, ionized, and electron-attached states having singlet to septet spin multiplicities, 1996.
- [36] B. Casper, D.A. Dixon, H.-G. Mack, S.E. Ulic, H. Willner, H. Oberhammer, *J. Am. Chem. Soc.* 116 (1994) 8319.
- [37] B. Casper, P. Lambotte, R. Minkwitz, H. Oberhammer, *J. Phys. Chem.* 97 (1993) 9992.
- [38] T.J. Lee, *J. Phys. Chem.* 99 (1995) 1943.
- [39] V. Morris, G.A. Walker, P. Jones, Y. Cao, S.C. Bhatia, J.H. Hall Jr., *J. Phys. Chem.* 93 (1989) 7071.
- [40] S.C. Bhatia, J.H. Hall Jr., *J. Chem. Phys.* 82 (1985) 1991.
- [41] L. Pauling, L.O. Brockway, *J. Am. Chem. Soc.* 59 (1937) 13.
- [42] M.T. Rayez, M. Destriau, *Chem. Phys. Lett.* 206 (1993) 278.
- [43] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, S. Iwata, *Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules*, Japan Scientific Societies Press, Tokyo, 1981.