

Fine Theoretical Spectroscopy Using SAC-CI General-*R* Method: Outer- and Inner-Valence Ionization Spectra of N₂O and HN₃

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Dedicated to Prof. Dr. Sigrid Doris Peyerimhoff on the occasion of her 65th birthday

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Fine theoretical spectroscopy for the outer- and inner-valence ionization spectra has been presented by using the SAC-CI (symmetry adapted cluster-configuration interaction) general-*R* method applied to N₂O and HN₃. The SAC-CI general-*R* method accurately simulated the experimental spectra and the detailed assignments of the satellite peaks were proposed. The continuous peaks *I* ~ *V* of N₂O observed by the dipole (*e,2e*) spectroscopy were finely reproduced. In particular, the low-lying satellites were calculated in good agreement with the experiment; two ²*Π* shake-up states at the foot of the *C* state, ²*Σ* and ²*Π* states for the peak *I*. For HN₃, new interpretation was proposed for the outer-valence region, namely, peaks 3 ~ 5 are composed of the mixture of the single-electron main peaks and the two-electron shake-up peaks. Inner-valence ionization spectrum of HN₃ was theoretically predicted for which no experimental spectrum has been reported.

1. Introduction

Accurate descriptions of excited and ionized states of molecules have long been a challenging subject in quantum chemistry. Chemistry involving these states has shown a rich variety of phenomena that were quite appealing but could not be fully understood without the knowledge of their electronic structure. However, it was generally believed to be difficult in 1970s to describe accurately the electronic structures of excited and ionized molecules because

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of their open-shell nature, high-energy nature, and the existence of many states in narrow energy region. Among various efforts, Peyerimhoff has established with Buenker the multi-reference CI (MR-CI) approach [1–10] and reported a lot of very accurate and extensive theoretical works on molecular spectroscopy involving electronic excitation spectrum [3], potential energy surfaces of the excited states [8], vibronic structure and the Renner–Teller effect [7, 11], spin-orbit effects including electron correlations [10], the lifetime of the electronically excited states [9], and so on. These studies have been summarized in more-than-four hundred research papers and she named it as theoretical spectroscopy [11]. These studies certainly constitute a milestone in theoretical spectroscopy and show an importance and utility of quantum chemistry in the studies of excited and ionized states of molecules and molecular systems.

A different approach for describing excited and ionized states was developed by the present author as SAC-CI (symmetry adapted cluster-configuration interaction) method [12–16]. The basis is to calculate first the electron correlation in the ground state accurately by the SAC method [17] and then describe the electron correlation in the excited state by modifying the ground-state correlation. This method is easier than calculating electron correlations separately for different electronic states and furthermore, a balanced result between the ground and excited (ionized) states is obtained. Further, by using SAC-CI general-*R* method [18–21], we can perform fine theoretical spectroscopy. We would like to dedicate an example of fine theoretical spectroscopy by calculating the ionization spectra of N_2O and HN_3 for celebrating the achievement established by Professor Sigrid Peyerimhoff.

Many of the excited and ionized states are described as one-electron processes from the ground state. However, there exist a lot of excited and ionized states that are characterized by two- or more-electron excitation processes. Satellite peaks that are observed in the valence-ionization spectrum are one such example and have attracted considerable interest since they contain the information of the electron correlations of molecules. Recently, fine analyses of these peaks have become possible due to the cooperative interplays between the qualified theoretical and experimental works.

Among the extensive works on the valence-ionization spectra of molecules, the inner-valence region of N_2O has been intensively studied by various spectroscopies, since there are many satellite peaks starting from relatively low energy region. For examples, the photoelectron spectroscopy (PES) using He II [22] and Al K_α [23] radiations, and dipole ($e,2e$) spectroscopy [24–26] have been reported. X-ray PES [27] was also reported with photon energies up to 120 eV and the assignments of the satellite peaks were discussed in comparison with other experimental and theoretical works. However, theoretical studies on the detailed analysis of the satellites have been very limited; only SAC-CI method [28] and 2ph-TDA (two-particle-hole Tamm–Dancoff approximation) method [25] were applied to the inner-valence region. It seems that

both of these calculations are now insufficient in the present level of computational technology.

On the other hand, the valence-ionized states of HN_3 have been much less investigated, though it is iso-electronic with N_2O . He I [29, 30] and He II PES [31] were applied to the gaseous HN_3 , however, inner-valence region was not examined except for the solid HN_3 [31]. Recently, detailed analysis was performed with the Penning ionization electronic spectroscopy (PIES) and He I UPS with the help of outer-valence Green's function (OVGF) calculations [32]. Theoretical study was limited only for the main peaks with perturbation theory [33]. Thus, it is worth presenting an accurate theoretical spectrum of this molecule and giving detailed assignments of the main and satellite peaks.

The SAC/SAC-CI method has now been well established as a useful quantum-chemical method for studying molecular ground, excited, ionized and electron attached states of molecules in singlet to septet spin-multiplicities [12–16, 34]. We can also calculate the energy gradient associated to these various electronic states [34–38]. For ordinary single electron excitation and ionization processes, we use SAC-CI SD(singles and doubles)-*R* method, but for multiple-electron processes like those involved in shake-up satellite peaks, the SD-*R* method is insufficient and the SAC-CI general-*R* method [18–21] has been shown to be a powerful tool. By the general-*R* method, we can not only describe accurately the multiple electron processes, but also calculate a large number of states appearing in the ionization spectra [39, 40]. Recently, we have applied systematically the general-*R* method to the outer- and inner-valence ionization spectra of several molecules [41–46] and gave detailed characterizations of the main and satellite peaks. In particular, we have given fine theoretical spectra of CO_2 [43], CS_2 and OCS [46] that are iso-electronic with N_2O and HN_3 studied in this paper. The molecules CO_2 , CS_2 and OCS have shown to have strong electron correlations and consequently to exhibit many shake-up states even from the outer-valence region. Thus, in this work, we investigate the ionization spectra of N_2O and HN_3 by the SAC-CI general-*R* method, aiming at the detailed and quantitative assignments of the satellite peaks appearing in the outer- and inner-valence regions.

2. Computational details

Vertical ionization spectra of N_2O and HN_3 were studied and the ground-state experimental geometries were used for the calculations; namely, $R_{\text{NN}} = 1.1282 \text{ \AA}$ and $R_{\text{NO}} = 1.1842 \text{ \AA}$ [47] for N_2O in $C_{\infty v}$ and $R_{\text{HN}(1)} = 1.015 \text{ \AA}$, $R_{\text{N}(1)\text{N}(2)} = 1.243 \text{ \AA}$, $R_{\text{N}(2)\text{N}(3)} = 1.134 \text{ \AA}$, $\angle\text{HN}(1)\text{N}(2) = \angle 108.8^\circ$, $\angle\text{N}(1)\text{N}(2)\text{N}(3) = \angle 171.3^\circ$ [48] for HN_3 in C_s . The basis set was selected as flexible to describe the electron correlations of the shake-up states, namely valence triple zeta (VTZ) of Ahlrichs [49]; $(10s6p)/[6s3p]$ GTOs for N and

O and $(5s)/[3s]$ for H augmented with two d -type polarization functions of $\zeta_d = 1.654, 0.469$ for N and $\zeta_d = 2.314, 0.645$ for O, one p -type polarization function of $\zeta_p = 0.8$ for H [50]. The resultant SCF dimensions were 81 and 87 for N_2O and HN_3 , respectively.

The ionization spectra of N_2O and HN_3 were calculated by the SAC-CI general- R method in both outer- and inner-valence regions. From the preliminary calculations, most of the shake-up states were shown to be dominantly described by two-electron processes, and therefore the R -operators were included up to triples. The $1s$ orbitals of N and O were kept as frozen core and all the other MOs were included in the active space; the SAC-CI active space consists of 8 occupied and 70 unoccupied MOs for N_2O , 8 occupied and 76 unoccupied MOs for HN_3 .

To reduce the computational effort, perturbation selection [28] was performed in the state-selection scheme. The threshold of the linked terms for the ground state was set to $\lambda_g = 1 \times 10^{-7}$ for N_2O and $\lambda_g = 1 \times 10^{-6}$ for HN_3 . The unlinked terms were described as the products of the important linked terms whose SD-CI coefficients were larger than 0.005. For ionized state, the thresholds of the linked doubles and triples were set to $\lambda_e = 1 \times 10^{-7}$ and $\lambda_e = 1 \times 10^{-6}$, respectively. The thresholds of the CI coefficients for calculating the unlinked operators in the SAC-CI method were 0.01 and 1×10^{-8} for the R and S operators, respectively.

The ionization cross-sections were calculated using the monopole approximation [51, 52] to estimate the relative intensities of the peaks. The degeneracy of the states involved is reflected in the intensity. For the calculations of monopole intensities, the correlated SAC/SAC-CI wave functions were used for the ground and ionized states to include both initial- and final-state correlation effects. Theoretical peaks were convoluted with the Gaussian envelopes to simulate the experimental spectrum. The envelopes are described by the Frank-Condon width and the resolution of the spectrometer. In the present calculation, the FWHM (Full Width at Half Maximum) of the Gaussian was determined so as to reproduce the line width of the main peak and used for all the calculated peaks. In the present calculation, the widths of $0.1 \times \Delta E$ and $0.05 \times \Delta E$ (in eV) were used for N_2O and HN_3 , respectively.

The SAC/SAC-CI calculations were executed using the SAC96 program system [53], which has been incorporated into the development version of the Gaussian suite of programs [34].

3. Results and discussions

3.1 N_2O

The ground state electronic structure of N_2O is described by $(\text{core})^6(4\sigma)^2(5\sigma)^2(6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^4$. The outer- and inner-valence regions of the ionization spectrum of N_2O up to *c.a.* 43 eV were studied by the SAC-CI general- R

method. For calculating the spectrum in this region, 80 and 60 solutions were obtained for ${}^2\Sigma$ and ${}^2\Pi$ symmetry, respectively. The perturbation selection was performed with the SDCI reference states and the resultant SAC-CI general-*R* dimensions were summarized in Table 1. In Fig. 1, the SAC-CI general-*R* spectrum was compared with the dipole (e,2e) spectrum [24]. Table 2 summarizes the IPs, monopole intensities, and main configurations of the outer- and inner-valence peaks, whose intensities are greater than 0.01 with several experimental IPs [22, 24, 25, 27].

Four main peaks were dominantly described by one-electron process; namely, $(2\pi)^{-1}$, $(7\sigma)^{-1}$, $(1\pi)^{-1}$, and $(6\sigma)^{-1}$, and they were observed at 12.89, 16.38, 18.24, and 20.11 eV, respectively, by the He II PES [22]. These states were accurately estimated by the previous SD-*R* calculation [28]. In the present work, their IPs were calculated as 12.64, 16.27, 18.25, and 20.05 eV for $X{}^2\Pi$, $A{}^2\Sigma$, $B{}^2\Pi$, and $C{}^2\Sigma$ states, respectively, in agreement with the experimental IPs. The intensity of the $B{}^2\Pi$ state was considerably distributed to the shake-up state through the interaction with $(2\pi^{-2}3\pi)$ as seen from the monopole intensity of 0.63, which was also obtained in the SAC-CI SD-*R* [28] and 2ph-TDA [25] works.

First shake-up state was calculated at 19.95 eV below the peak C and was characterized as $(2\pi^{-2}3\pi)$. This state was not identified by the dipole (e,2e) [24–26], but was detected with the He II PES [22] by Potts and Williams at 19.5 eV. The relative intensity of this satellite to $B{}^2\Pi$ state was calculated to be 0.147, which is compared with the experimental ratio of 0.125 [22]. Another ${}^2\Pi$ state of the same ionization character was obtained at 21.57 eV.

Peak I was observed at 24.0 eV [24] by the dipole (e,2e) spectroscopy, and later this peak was reported to be composed of the two components at 23.7 and 24.5 eV [25]. These peaks were attributed to the ${}^2\Sigma$ and ${}^2\Pi$ states calculated at 23.95 and 25.49 eV, respectively, whose assignments were the same as the dipole (e,2e) work [25] with the help of the 2ph-TDA calculation. These states are characterized as $(7\sigma^{-1}3\pi2\pi^{-1})$ and $(2\pi^{-2}3\pi)$. The intensity of the ${}^2\Pi$ state is calculated to be larger than that of ${}^2\Sigma$ state by three times, which agrees with

Table 1. SAC-CI general-*R* dimensions for the ionized states of N_2O and HN_3 .

	singles	doubles	triples	total
N_2O				
${}^2\Sigma$	4	1239	120 867	122 110
${}^2\Pi$	2	1034	102 847	103 883
HN_3				
${}^2A''$	6	2475	100 273	102 754
${}^2A''$	2	2000	75 939	77 941

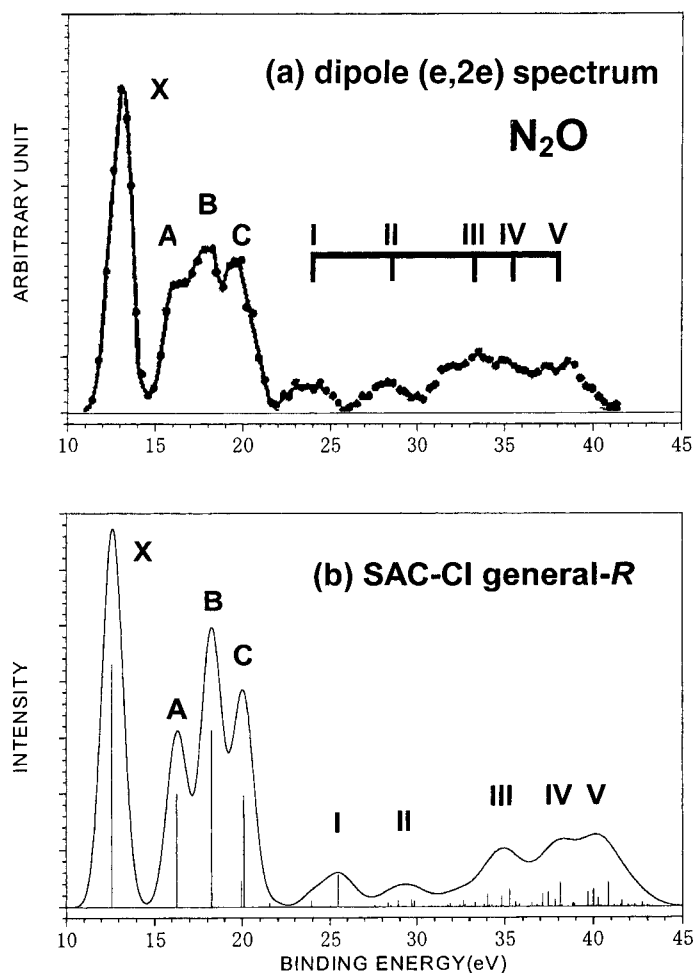


Fig. 1. Valence ionization spectra of N₂O by (a) dipole (e,2e) [24] and (b) the SAC-CI general-*R* method.

the experimental ratio; the relative intensities of 0.02 and 0.06 were reported for the peaks at 22.6 and 24.1 eV by the He II PES [22], though the intensity of He II PES does not directly reflect the pole strength. Peak II was observed at 28.5 eV by dipole (e,2e) [24] and 28.7 eV by He II PES [22]. For this band, three $^2\Sigma$ states and one $^2\Pi$ state was calculated at 28.34, 28.93, 29.69, and 29.85 eV with the total pole strength of 0.15. Unfortunately, the relative intensity was not reported for this band by the dipole (e,2e), whose cross sections can be compared with the pole strength.

Peak III observed at 33.0 and 33.7 eV by the dipole (e,2e) [24] and He II PES [22], respectively, were dominantly assigned to the $^2\Sigma$ states. Six $^2\Sigma$ states and one $^2\Pi$ state with the considerable intensity were obtained in this energy region with the total intensity of 0.43. Fantoni *et al.* [26] identified the Π structure for the peaks at 26.0 and 33.0 eV with the dipole (e,2e) spectroscopy. Accordingly, two $^2\Pi$ states were calculated at 25.49 and 31.90 eV,

Table 2. Ionization potentials (IPs) (in eV), monopole intensities, and main configurations of the valence ionized states of N₂O calculated by the SAC-CI general-*R* method.

dipole (e,2e) ^a		He II		diopole		X-ray		SAC-CI general- <i>R</i>	
No.	I.P.	PES ^b	(e,2e) ^c	PES ^d	I.P.	Intensity	State	Main configuration	($ C > 0.3$)
X		12.89			12.64	0.862	² Π	0.91(2π ⁻¹)	
A		16.38			16.27	0.794	² Σ	0.84(7σ ⁻¹)	
B		18.24			18.25	0.629	² Π	0.76(1π ⁻¹) + 0.41(2π ⁻² 3π)	
		19.5			19.95	0.093	² Π	0.76(2π ⁻² 3π) + 0.32(2π ⁻² 3π)	
C		20.11			20.05	0.788	² Σ	0.85(6σ ⁻¹)	
					21.57	0.013	² Π	0.76(2π ⁻² 3π) - 0.38(2π ⁻² 3π) + 0.33(2π ⁻² 3π)	
I	24.0	22.6	23.7	23.5	23.95	0.043	² Σ	0.72(7σ ⁻¹ 3π2π ⁻¹) + 0.69(7σ ⁻¹ 3π2π ⁻¹) + 0.32(2π ⁻¹ 3π7σ ⁻¹) + 0.31(2π ⁻¹ 3π7σ ⁻¹)	
		24.1	24.5		25.49	0.111	² Π	-0.31(1π ⁻¹) + 0.60(2π ⁻² 3π) + 0.38(2π ⁻² 3π)	
II	28.5	28.7	28.5	28.0	28.34	0.015	² Π	0.66(7σ ⁻¹ 8σ2π ⁻¹) + 0.38(2π ⁻¹ 8σ7σ ⁻¹) - 0.34(7σ ⁻¹ 5π2π ⁻¹) + 0.32(7σ ⁻¹ 8σ1π ⁻¹) - 0.32(7σ ⁻¹ 9σ2π ⁻¹)	
					28.93	0.045	² Σ	0.40(2π ⁻¹ 3π7σ ⁻¹) + 0.38(2π ⁻¹ 3π7σ ⁻¹) - 0.34(6σ ⁻¹ 3π2π ⁻¹) - 0.34(6σ ⁻¹ 3π2π ⁻¹)	
					29.69	0.045	² Σ	0.56(7σ ⁻¹ 3π1π ⁻¹) + 0.38(7σ ⁻¹ 3π1π ⁻¹)	
					29.85	0.041	² Σ	0.36(2π ⁻¹ 8σ1π ⁻¹) + 0.32(2π ⁻¹ 8σ1π ⁻¹)	

though the intensity of the latter state was small. Peaks IV and V were attributed to the (5σ)⁻¹ and (4σ⁻¹) states, respectively, which strongly interact with the shake-up states. These peaks were observed at 35.5 and 38.0 eV by the dipole (e,2e) [24] and 35.5 and 38.5 eV by the X-ray PES [27]. For the

Table 2. continued.

dipole (e,2e) ^a		He II		X-ray		SAC-CI general-R		
No.	I.P.	PES ^b	diopole (e,2e) ^c	PES ^d	I.P.	Intensity	State	Main configuration ($ C > 0.3$)
III	33.0	33.7	(~ 33.5)	33.0	31.90	0.012	$^2\Pi$	$0.39(7\sigma^{-1}3\pi6\sigma^{-1}) - 0.36(2\pi^{-1}3\pi1\pi^{-1}) - 0.33(2\pi^{-1}3\pi1\pi^{-1})$
					32.66	0.039	$^2\Sigma$	$0.46(1\pi^{-1}8\sigma2\pi^{-1}) + 0.46(1\pi^{-1}8\sigma2\pi^{-1}) + 0.34(2\pi^{-1}8\sigma1\pi^{-1}) + 0.33(2\pi^{-1}8\sigma1\pi^{-1})$
					33.34	0.022	$^2\Sigma$	$0.54(7\sigma^{-1}8\sigma6\sigma^{-1}) - 0.42(7\sigma^{-1}5\pi6\sigma^{-1})$
					34.31	0.102	$^2\Sigma$	$0.34(1\pi^{-1}3\pi7\sigma^{-1}) + 0.34(1\pi^{-1}3\pi7\sigma^{-1})$
					34.85	0.124	$^2\Sigma$	$0.31(5\sigma^{-1}) - 0.40(6\sigma^{-1}8\sigma7\sigma^{-1})$
					35.28	0.110	$^2\Sigma$	$0.49(6\sigma^{-1}3\pi1\pi^{-1}) + 0.48(6\sigma^{-1}3\pi1\pi^{-1}) + 0.31(7\sigma^{-1}10\sigma2\pi^{-1})$
IV					35.86	0.018	$^2\Sigma$	$0.34(2\pi^{-2}5\pi) + 0.33(2\pi^{-2}5\pi) - 0.31(2\pi^{-2}4\pi) - 0.30(2\pi^{-2}4\pi)$
	35.5	37.3	(~ 36)	35.5	36.55	0.028	$^2\Sigma$	$0.32(7\sigma^{-1}8\sigma6\sigma^{-1})$
					35.62	0.031	$^2\Sigma$	$0.62(7\sigma^{-1}10\sigma2\pi^{-1}) + 0.62(7\sigma^{-1}4\pi2\pi^{-1}) - 0.30(2p10\sigma7\sigma)$
					37.08	0.082	$^2\Sigma$	$0.44(6\sigma^{-1}8\sigma7\sigma^{-1}) - 0.36(2\pi^{-1}4\pi7\sigma^{-1}) + 0.36(2\pi^{-1}10\sigma7\sigma^{-1})$
					37.59	0.052	$^2\Sigma$	$0.43(2\pi^{-2}12\sigma) + 0.42(2\pi^{-2}12\sigma)$
					37.84	0.052	$^2\Sigma$	$0.35(1\pi^{-2}8\sigma) + 0.35(1\pi^{-2}8\sigma)$
				38.30	0.234	$^2\Sigma$	$0.45(5\sigma^{-1}) + 0.35(2\pi^{-2}12\sigma) + 0.34(2\pi^{-2}12\sigma)$	

peak IV, six $^2\Sigma$ states were calculated and the intensity of these states were mainly due to the final-state interaction with the $(5\sigma)^{-1}$ state; total pole strength was calculated to be 0.48. For the peak V and its shoulder in the higher energy region about ~ 42 eV [25], ten $^2\Sigma$ states with the intensity larger than 0.01

Table 2. continued.

dipole (e,2e) ^a		He II		X-ray		SAC-CI general-R		
No.	I.P.	PES ^b	diopole (e,2e) ^c	PES ^d	I.P.	Intensity	State	Main configuration ($ C > 0.3$)
V	38.0		(~ 39)	38.5	39.68	0.096	$^2\Sigma$	$0.36(1\pi^{-1}3\pi6\sigma^{-1}) + 0.36(1\pi^{-1}3\pi6\sigma^{-1})$
					40.00	0.129	$^2\Sigma$	$0.34(4\sigma^{-1})$
					40.22	0.057	$^2\Sigma$	$0.49(2\pi^{-1}11\sigma7\sigma^{-1}) + 0.40(2\pi^{-1}5\pi7\sigma^{-1})$
					40.86	0.183	$^2\Sigma$	$0.41(4\sigma^{-1})$
					41.79	0.028	$^2\Sigma$	$0.52(2\pi^{-2}3\pi^27\sigma^{-1}) + 0.40(2\pi^{-2}3\pi^27\sigma^{-1})$
					41.86	0.015	$^2\Sigma$	$0.35(2\pi^{-2}3\pi^27\sigma^{-1}) + 0.31(2\pi^{-2}3\pi^26\sigma^{-1})$
					41.87	0.016	$^2\Sigma$	$0.35(1\pi^{-1}10\sigma7\sigma^{-1}) - 0.35(1\pi^{-1}4\pi7\sigma^{-1})$
					42.24	0.021	$^2\Sigma$	$+0.32(7\sigma^{-1}4\pi1\pi^{-1}) - 0.31(7\sigma^{-1}10\sigma1\pi^{-1})$
			(~ 42)		42.25	0.012	$^2\Sigma$	$0.33(2\pi^{-1}4\pi6\sigma^{-1})$
					42.92	0.010	$^2\Sigma$	$0.39(1\pi^{-1}12\sigma2\pi^{-1}) + 0.37(1\pi^{-1}12\sigma2\pi^{-1})$
								$-0.33(2\pi^{-1}12\sigma1\pi^{-1}) - 0.30(2\pi^{-1}12\sigma1\pi^{-1})$
								$0.34(2\pi^{-1}3\pi5\sigma^{-1}) + 0.33(5\sigma^{-1}3\pi2\pi^{-1})$
								$-0.35(2\pi^{-1}3\pi7\sigma^{-1}3\pi2\pi^{-1})$
								$0.35(5\sigma^{-1}3\pi2\pi^{-1}) + 0.49(2\pi^{-2}3\pi^27\sigma^{-1})$
								$+0.39(2\pi^{-2}3\pi^27\sigma^{-1}) + 0.37(2\pi^{-2}3\pi^27\sigma^{-1})$

^a [24]; ^b [22]; ^c [25]; ^d [27]

were assigned. The double ionization threshold of N₂O has been determined by the double-charge-transfer (DCT) spectroscopy [54, 55] and photoion-photoion coincidence spectroscopy (PIPICO) [55]: triplet states of N₂O²⁺ were measured at 35.7, 38.8, 41.8, and 43.1 eV [54].

3.2 HN₃

The ground-state electronic structure of HN₃ is (core)⁶(4a')²(5a')²(6a')²(7a')²(1a'')²(8a')²(9a')²(2a'')². The valence-ionization spectrum of HN₃ up to about 35 eV, whose energy region corresponds to peaks I~III of N₂O were studied. For this purpose, 80 and 60 states were calculated for A' and A'' symmetry, respectively. The number of single, double, and triple R-operators were summarized in Table 1; SAC-CI dimensions were 102754 and 77941 for A' and A'' states, respectively. Fig. 2 shows the valence-ionization spectrum of HN₃ calculated by the SAC-CI general-R method in comparison with the He I UPS [32]. Unfortunately, there is no experimental spectrum for the inner-valence region of HN₃, except for solid phase. Table 3 summarizes the IPs, monopole intensities, and main configurations of the outer- and inner-valence peaks, whose intensities are greater than 0.01.

The theoretical spectrum by the SAC-CI general-R method reproduced the peak positions and shape of the experimental spectrum. Six peaks exist

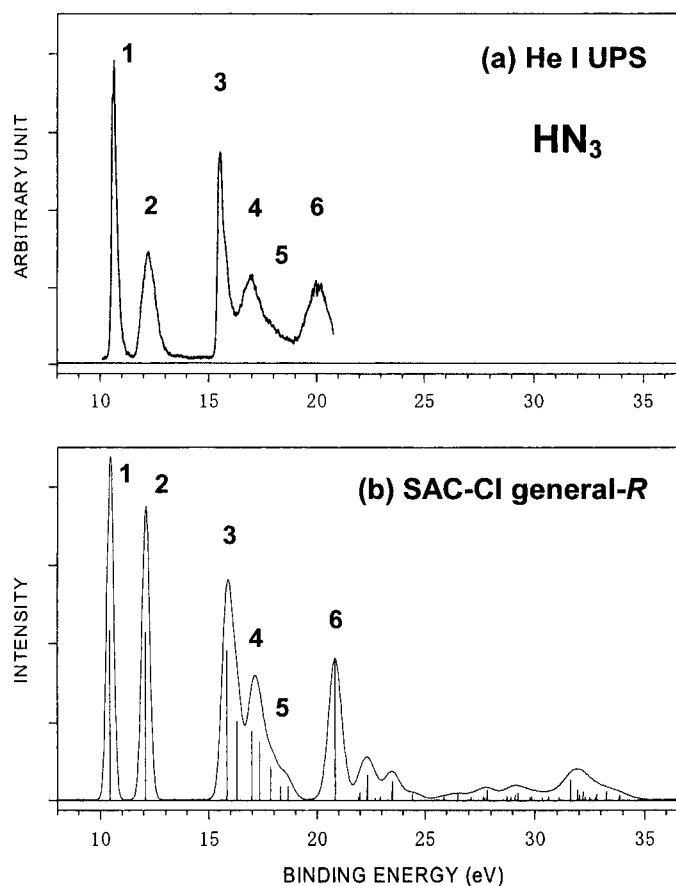


Fig. 2. Valence ionization spectra of HN₃ by (a) He I UPS [32] and (b) SAC-CI general-R method.

Table 3. Ionization potentials (IPs) (in eV), monopole intensities and main configurations of the valence ionized states of HN_3 calculated by the SAC-CI general-*R* method.

He I UPS ^a		SAC-CI general- <i>R</i>			
No.	I.P.	I.P.	Intensity	State	Main configuration ($ C > 0.3$)
1	10.73	10.45	0.867	$2A''$	$0.91(2a''^{-1})$
2	12.28	12.10	0.857	$2A'$	$0.90(9a'^{-1})$
3	15.53	15.84	0.765	$2A'$	$0.79(8a'^{-1})$
4	16.92	16.30	0.408	$2A''$	$0.62(1a''^{-1}) - 0.59(2a''^{-2}3a'')$
		16.98	0.358	$2A'$	$0.55(7d'^{-1}) - 0.53(2a''^{-2}10a') + 0.32(2a''^{-2}11a')$
		17.35	0.303	$2A'$	$+0.32(2a''^{-1}3a'9a'^{-1})$
5	17.7	17.85	0.166	$2A''$	$0.49(7d'^{-1}) + 0.52(2a''^{-2}10a') - 0.35(2a''^{-2}11a')$
		18.32	0.069	$2A''$	$-0.40(1a''^{-1}) + 0.70(2a''^{-1}10a'9a'^{-1}) - 0.43(2a''^{-1}11a'9a'^{-1})$
		18.66	0.067	$2A'$	$0.67(9d'^{-1}10a'2a'^{-1}) + 0.49(2a''^{-2}3a'')$
					$-0.43(9a'^{-1}11a'2a''^{-1}) + 0.41(2a''^{-1}10a'9a'^{-1})$
					$0.91(9d'^{-1}3a'2a''^{-1})$

in the outer-valence region of the He I UPS [32]. There is a correspondence of the electronic structure between HN_3 and N_2O , however, large difference has been found between their valence-ionization spectra as shown in Fig. 1 and 2. The peaks 1 and 2 are ionization from the $2a''$ and $9a'$ orbitals, respectively, and they correspond to the peak X of N_2O . They were calculated at 10.45 and 12.10 eV with the energy separation of 1.55 eV in good agreement with the experiment. The peak 2 was experimentally observed as a broad peak, which should be attributed to the vibrational structure. $2a''$ orbital is a non-bonding MO localized on N(1) and N(3) atoms, while $9a'$ orbital is delo-

Table 3. continued.

He I UPS ^a		SAC-CI general-R			
No.	I.P.	I.P.	Intensity	State	Main configuration ($ C > 0.3$)
6	19.91	20.85	0.710	$^2A'$	$0.80(6a'^{-1})$
		21.94	0.015	$^2A''$	$0.59(8a'^{-1}10a'2a''^{-1}) - 0.42(2a''^{-1}10a'7a'^{-1})$ $- 0.40(7a'^{-1}10a'2a''^{-1}) + 0.36(8a''^{-1}11a'2a''^{-1})$
		21.99	0.037	$^2A'$	$0.31(1a''^{-1}10a'2a''^{-1}) - 0.29(2a''^{-1}10a'1a'^{-1})$
		22.32	0.060	$^2A'$	$0.75(8a'^{-1}3a'2a''^{-1})$
		22.36	0.125	$^2A''$	$-0.34(1a''^{-1}) + 0.52(9a'^{-1}10a'2a''^{-1})$ $- 0.35(2a''^{-2}3a'')$
		22.72	0.027	$^2A''$	$0.42(9a'^{-1}11a'2a''^{-1}) - 0.36(2a''^{-1}11a'9a'^{-1})$
		22.78	0.012	$^2A'$	$0.69(7a'^{-1}3a'2a''^{-1}) + 0.51(9a'^{-1}3a'1a'^{-1})$ $+ 0.49(2a''^{-1}3a'7a'^{-1}) + 0.39(1a''^{-1}3a'9a'^{-1})$
		22.94	0.017	$^2A'$	$0.66(8a'^{-1}10a'9a'^{-1}) - 0.41(8a'^{-1}11a'9a'^{-1})$
		23.48	0.049	$^2A''$	$0.35(1a''^{-1}3a'2a''^{-1}) - 0.32(7a'^{-1}10a'2a''^{-1})$
		23.50	0.098	$^2A'$	$0.50(2a''^{-1}3a'9a'^{-1}) + 0.40(7a'^{-1}3a'2a''^{-1})$
		24.45	0.038	$^2A'$	$0.33(2a''^{-1}3a'9a'^{-1}) + 0.32(2a''^{-1}3a'7a'^{-1})$ $- 0.31(7a'^{-1}10a'9a'^{-1})$
		25.90	0.016	$^2A'$	$0.72(9a'^{-1}3a'1a'^{-1}) - 0.48(7a'^{-1}3a'2a''^{-1})$
		26.53	0.029	$^2A'$	$0.45(2a''^{-1}3a'8a'^{-1}) - 0.39(8a'^{-2}10a')$
		27.68	0.014	$^2A'$	$0.40(6a'^{-1}3a'2a''^{-1}) + 0.30(1a''^{-1}11a'2a''^{-1})$

calized over HN_3 molecule and has a bonding character. Hence, the equilibrium structure of $(9a')^{-1}$ is different from the ground state so that the vibrational structure should be remarkable for peak 2 and is responsible for the broad peak.

Peak 3 observed at 15.53 eV was assigned to the $(8a')^{-1}$ state by the PIES experiment [32]. However, the $(1a'')^{-1}$ state interacting with $(2a''^{-2}3a'')$ was also obtained just above $(8a')^{-1}$ state in our calculation, and we attributed these two states to the peak 3. For the next peak 4 observed at 16.92 eV, twinning peaks of $(7a')^{-1}$ were calculated at 16.98 and 17.35 eV; these states were described by the linear combination of $(7a')^{-1}$, $(2a''^{-2}10a')$, and $(2a''^{-2}11a')$. As the shoulder of peak 4, peak 5 was measured at 17.7 eV [32] and this peak was attributed to the satellites by the analysis of the collision energy dependence of partial ionization cross section (CEDPICS) of the PIES [32]. Accordingly, three shake-up states of both A' and A'' symmetry were calculated at 17.85,

Table 3. continued.

He I UPS ^a		SAC-CI general- <i>R</i>			
No.	I.P.	I.P.	Intensity	State	Main configuration ($ C > 0.3$)
		27.13	0.015	² A'	$0.38(2a''^{-2}13a') + 0.34(2a''^{-1}12a') + 0.33(2a''^{-1}3a''7d^{-1}) - 0.33(1a''^{-1}3a''9a'^{-1})$
		27.75	0.010	² A'	$0.49(6a'^{-1}3a''2a''^{-1})$
		27.84	0.049	² A'	$0.37(8a''^{-2}10a') - 0.37(9a'^{-1}10a'8a'^{-1})$
		28.75	0.020	² A'	$0.32(6a'^{-1}10a'9a'^{-1})$
		28.92	0.014	² A''	$0.43(2a''^{-1}3a''1a''^{-1}) - 0.41(9a'^{-1}10a'1a'^{-1})$
		29.12	0.025	² A'	$0.38(9a'^{-1}10a'7d^{-1}) - 0.32(7d'^{-1}11a'9a'^{-1})$
		29.24	0.037	² A'	$0.41(6a'^{-1}10a'8a'^{-1}) + 0.37(8a'^{-1}10a'7a'^{-1}) + 0.33(2a''^{-1}3a''6a'^{-1})$
		29.80	0.013	² A'	$0.34(7a'^{-1}10a'8a'^{-1}) + 0.28(8a'^{-1}3a''1a'^{-1})$
		29.87	0.020	² A'	$0.40(8a'^{-1}3a''1a''^{-1}) - 0.37(9a'^{-1}4a''2a''^{-1}) - 0.35(6a'^{-1}10a'9a'^{-1}) - 0.31(1a''^{-1}3a''9a'^{-1})$
		30.36	0.015	² A'	$0.51(8a'^{-1}3a''1a''^{-1}) + 0.32(1a''^{-1}3a''8a'^{-1})$
		30.64	0.020	² A'	$0.27(2a''^{-1}11a'1a''^{-1})$
		31.12	0.014	² A'	$0.44(8a'^{-1}14a'9a'^{-1}) + 0.40(9a'^{-1}14a'8a'^{-1}) + 0.36(2a''^{-1}4a''9a'^{-1})$
		31.63	0.103	² A'	$0.31(5a'^{-1})$
		31.95	0.054	² A'	$0.32(9a'^{-2}15a')$

18.32, and 18.66 eV. Peaks 3 ~ 5 of HN₃ correspond to the peaks A and B of N₂O, however, the assignment of the outer-valence region of HN₃ is very characteristic due to the strong electron correlations: this picture is very different from the previous experimental [32] and theoretical [33] works. Peak 6 was attributed to the $(6a')^{-1}$ state in agreement with the experimental assignment. This peak corresponds to the peak C of N₂O.

Above this energy region, no experimental information exists for the gas phase HN₃. In our calculation, many correlation peaks were calculated in the inner-valence region and their IPs were relatively lower than corresponding states of N₂O. The shake-up states in the energy region of 22 ~ 24 eV were assigned to the satellites of $(7a')^{-1}$ and $(1a'')^{-1}$, which correspond to the peak I of N₂O; remarkable A'' and A' state were calculated at 22.36 and 23.50 eV, respectively. The shake-up states with small intensity continue from 27 to 30 eV, whose intensity originates in $(6a')^{-1}$; these peaks correspond to the peak II of

Table 3. continued.

He I UPS ^a		SAC-CI general- <i>R</i>			
No.	I.P.	I.P.	Intensity	State	Main configuration ($ C > 0.3$)
	32.03		0.026	² A'	0.48(2a'' ⁻² 16a') + 0.32(9a'' ⁻¹ 5a''2a'' ⁻¹)
	32.20		0.042	² A'	0.36(9a'' ⁻¹ 5a''2a'' ⁻¹)
	32.30		0.015	² A'	0.44(9a'' ⁻¹ 5a''2a'' ⁻¹) - 0.40(9a'' ⁻² 15a')
	32.51		0.013	² A'	0.42(9a'' ⁻¹ 11a'7a'' ⁻¹) + 0.34(7d'' ⁻¹ 14a'9a'' ⁻¹)
	32.76		0.011	² A'	0.39(2a'' ⁻² 16a') - 0.32(2a'' ⁻¹ 13a'1a'' ⁻¹) -0.31(1a'' ⁻¹ 14a'2a'' ⁻¹) + 0.28(1a'' ⁻¹ 12a'2a'' ⁻¹)
	32.81		0.030	² A'	0.28(9a'' ⁻¹ 11a'6a'' ⁻¹)
	33.27		0.043	² A'	0.53(2a'' ⁻² 18a') + 0.35(8a'' ⁻¹ 4a''2a'' ⁻¹)
	33.84		0.014	² A'	0.41(9a'' ⁻¹ 11a'6a'' ⁻¹) + 0.34(6a'' ⁻¹ 11a'9a'' ⁻¹)
	33.88		0.024	² A'	0.61(2a'' ⁻¹ 4a''8a'' ⁻¹) + 0.50(8a'' ⁻¹ 4a''2a'' ⁻¹) -0.33(6a'' ⁻¹ 3a''1a'' ⁻¹)

^a [32].

N₂O. For the energy region of 30 ~ 35 eV, shake-up states of (5a')⁻¹ exist and they correspond to the peak III of N₂O.

4. Conclusions

The SAC-CI general-*R* method has been utilized for calculating the fine theoretical spectra of the valence-ionizations of N₂O and HN₃. The peak positions and shape of the experimental spectra were well reproduced and the detailed assignments of the satellite peaks were proposed.

For N₂O, the general-*R* method gave the continuous satellite peaks in the energy region of 24 ~ 43 eV, which reproduced the peaks I ~ V observed by the dipole (e,2e) spectroscopy. Low-lying satellites for which earlier theoretical

results were criticized by the X-ray PES work [27] were calculated in agreement with the experiment; two ${}^2\Pi$ shake-up states at the foot of *C* state, ${}^2\Sigma$ and ${}^2\Pi$ states for the peak I. For peaks II ~ V, many ${}^2\Sigma$ satellites were calculated with distributed intensity and no prominent peaks were obtained, which is different from the previous theoretical works [25, 28]. Some ${}^2\Pi$ states were calculated in the peaks I ~ III, i.e. 25.49, 28.34, and 31.90 eV, which agrees with the experimental observations [25, 27].

For HN_3 , new interpretation was proposed for the peaks in the outer-valence region; the peaks 3 ~ 5 were composed of the mixture of the one- and two-electron processes and therefore, split peaks. The satellite spectrum in the inner-valence region which corresponds to the peaks I ~ III was calculated for which no experimental spectrum was reported.

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