

GEOMETRY RELAXATIONS AFTER INNER-SHELL EXCITATIONS AND IONIZATIONS

Masahiro EHARA^{a,c,*} and Hiroshi NAKATSUJI^{b,c,*}

^a Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan; e-mail: ehara@sbchem.kyoto-u.ac.jp

^b Quantum Chemistry Research Institute, Kyodai Katsura Venture Plaza 106, Goryo Oohara 1-36, Nishikyo-ku, Kyoto 615-8245, Japan; e-mail: h.nakatsuji@qcri.or.jp

^c JST, CREST, Sanbancho-5, Chiyoda-ku, Tokyo 102-0075, Japan

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Dedicated to Professor Rudolf Zahradník on the occasion of his 80th birthday.

The geometry relaxations due to the inner-shell excitations and ionizations have been studied by the SAC-CI method. The characteristic molecular geometry changes were predicted for the core-hole states of CH₄, NH₃, H₂O and HF: the calculated CH bond length change agrees well with the result simulated by the observed spectrum. The C1s excitation spectrum of CH₄ was also investigated for the Rydberg states of the principal quantum numbers $n = 3, 4$ and 5 . The potential energy curves of the dipole-allowed excited states were calculated for the totally symmetric stretching mode. The vibrational structure and Franck–Condon factors for the C1s excitation spectrum were well reproduced, which shows that the equilibrium geometries of the excited states were accurately evaluated. The geometries of the inner-shell π^* excited states of N₂O and CO₂ were also examined. The calculated geometries of these states qualitatively agreed with the experimental values of the corresponding equivalent-core molecules.

Keywords: Core-electron process; Electronic structure; SAC-CI; Geometry optimization; Vibrational spectrum.

Molecules show characteristic geometry changes in the inner-shell excited and ionized states, although the core electrons do not directly participate in the chemical bonding^{1,2}. The characteristic geometries can be observed as the vibrational spectra by photoexcitation spectroscopy. They also play an important role in the dynamics of the Auger electron processes. Recently,

+ Present address: Institute for Molecular Science, Okazaki 444-8585, Japan; e-mail: ehara@ims.ac.jp

much efforts have been devoted to probe the geometrical changes by experiment¹. However, for interpreting these spectra and excited-state dynamics, accurate theoretical information on the molecular structure in the core-excited and ionized states is indispensable.

For the core-electronic states, Bagus and Schaefer performed pioneering theoretical works using the Hartree-Fock method. They calculated the core-electron binding energies (CEBEs) of some diatomic molecules like NO and O₂^{3,4}. After their works, many theoretical works challenged the inner-shell electronic processes. In these works, electron correlation and core-valence correlation have been found to be important for describing the inner-shell excited and ionized states accurately.

The SAC (symmetry-adapted cluster)⁵/SAC-CI (configuration interaction) method^{6,7} has been established as a reliable and useful tool for investigating a wide variety of chemistry⁸⁻¹⁰. The analytical energy gradient of this method has also been developed¹¹⁻¹⁴ and, therefore, the geometry relaxation and the chemical reaction dynamics can be studied. Recently, we have successfully applied the SAC-CI method to various kinds of core-electron processes: the CEBE¹⁵, the inner-shell ionization satellite spectra of CH₄, NH₃¹⁵, H₂O¹⁶, formaldehyde¹⁷, and the vibrational spectrum of the core-hole state of H₂O¹⁸. The g-u splitting of homonucleus molecules like N₂, C₂H₂, C₂H₄ and C₂H₆ has been well predicted¹⁵. The overlapping vibrational spectra of the low-lying shake-up satellite states of CO¹⁹ and N₂²⁰ were also successfully interpreted by the present method; the potential energy curves of the inner-shell shake-up states were accurately calculated.

In the core-electron processes, the orbital relaxation is much larger in comparison with the valence electron processes. Recently, for treating this effect, the valence universal coupled cluster method for open-shell systems has been developed by Jana and Mukherjee²¹. This method can describe both the orbital relaxation and the correlation relaxation accompanying ionization/excitation efficiently and explicitly in a spin-free manner. The method was applied to the core- and the inner- and outer-valence ionization potentials of H₂O, NH₃ and CH₄, and Ne.

The open-shell reference (OR)-SAC-CI method²² has also been developed for investigating the open-shell systems. In this method, orbital relaxation due to the core-electron process is directly described in the reference function. Therefore, this method describes the core-excited and ionized states more efficiently than the method starting from the closed-shell reference function. The method has been shown to be useful for calculating the core-electron binding energy, i.e. the main line and satellite spectra of inner-shell ionizations.

In the present study, we investigated the geometry relaxation due to the inner-shell excitations and ionizations by the SAC-CI method. The analytical energy gradient of the method was used to calculate the geometries of the core-hole states of CH₄, NH₃, H₂O and HF. The C1s excitation spectrum of CH₄, for which the vibrational structure was observed, was simulated by calculating the potential energy curves for the totally symmetric stretching mode. The molecular structures of the core-excited states of N₂O and CO₂ were also studied. The results are compared with the experimental data and the equivalent core model.

COMPUTATIONAL DETAILS

The core-excited and ionized states were calculated by the SAC-CI general-*R* method. The flexible basis sets were used to allow the description of the orbital reorganization and electron correlations; For calculating core-hole states of CH₄, NH₃, H₂O and HF, cc-pCVTZ [6s5p3d/3s2p] were used, namely, correlation-consistent valence triple zeta [4s3p2d/3s] augmented with [2s2p1d] describing the core-valence polarization. For calculating the core-excitation spectrum of CH₄, [6s4p1d/3s1p] whose core-part contraction was split from Huzinaga–Dunning [5s3p1d/3s1p] basis sets^{23,24} and augmented with the Rydberg functions [5s5p5d] proposed by Kaufmann et al.²⁵; the [11s9p6d] basis set was used. For N₂O and CO₂, the VTZ1P basis set by Ahlrichs' group²⁶ [5s3p1d] was used. In the SAC-CI calculation, single to triple *R*-operators were included to describe the electron correlations and orbital relaxation; triples are necessary for describing orbital relaxations as well as electron correlations. For reference orbitals, the ground-state Hartree–Focks with canonical MOs were used; core-localized orbitals were not adopted. All MOs were included in the active space to describe core-hole relaxation.

To reduce the computational requirements the perturbation selection procedure was adopted²⁷. The threshold of the linked terms for the ground state was set to 1.0×10^{-6} a.u. and the unlinked terms were adopted as the products of the important linked terms with SD-CI coefficients greater than 0.005. For the inner-shell excited and ionized states, all the single and double operators were included without selection and the threshold of the higher triples was set to 1.0×10^{-7} a.u. The reference functions of the perturbation selection were chosen from the SD-CI solutions. The thresholds of the CI coefficients for calculating the unlinked operators in the SAC-CI method were 0.05 and 0.0 for the *R* and *S* operators, respectively.

For evaluating the vibrational states of the excitation spectrum of CH_4 , the potential energy curves were calculated for the symmetric stretching mode. The calculated potential curves were fitted with 8th-order extended Rydberg functions and vibrational analysis was performed. For simulating the photoelectron spectrum, vibrational wave functions and Franck-Condon factors were calculated by the grid method.

The SAC/SAC-CI calculations were executed with the Gaussian03 suite of programs²⁸ with some modifications for calculating inner-shell excited and ionized states.

RESULTS AND DISCUSSION

Geometry of the Core-Hole State of CH_4 , NH_3 , H_2O and HF

The calculated bond length change by the C1s ionization of CH_4 is compared with the experimental values^{29–32} and other theoretical values^{29,33,34} in Table I. The experimental values were evaluated by simulating the vibrational spectrum observed in XPS^{29–32}. The values calculated by the equivalent core model are also given for comparison. The RHF calculations tend to evaluate a large geometrical change for this core-ionized state. The equivalent

TABLE I
Change of CH bond length of CH_4 by core ionization

Method	Basic set	ΔR_{CH} , Å
Equivalent core		
RHF ^a	6-311G(d,p)	-0.072
MP4 ^a	6-311G(d,p)	-0.068
CCSD(T) ^b	TZ(2df,2pd)	-0.064
CCSD ^c	[4s3p2d1f/3s2p1d]	-0.067
Hole state		
RHF ^d	[7s5p3d/3s2p]	-0.056
CAS ^d	[5s4p3d/3s1p]	-0.053
CCI ^d	[5s4p3d/3s1p]	-0.041
SAC-CI ^c	[6s5p3d/3s2p]	-0.053
Experimental		-5.0 ^a , -5.3 ^e , -4.7 ^f , -4.8 ^g

^a Ref.²⁹; ^b ref.³³; ^c this paper; ^d ref.³⁴; ^e ref.³⁰; ^f ref.³¹; ^g ref.³²

lent core model also estimated the geometry relaxation larger, namely $\Delta R = -0.068$, -0.067 and -0.064 Å by MP4²⁹, CCSD and CCSD(T)³³, respectively, though the electron correlations are included. On the other hand, the theoretical values by calculating the core-hole state directly are in good agreement with the experimental ones. The present calculation predicted the value of $\Delta R = -0.053$ Å in comparison with the experimental values, $\Delta R = -0.047$ – (-0.053) Å. The CAS and MCPDF calculations also gave similar relaxation of $\Delta R = -0.053$ and -0.049 Å, respectively^{29,34}.

Table II summarizes the geometries and adiabatic ionization energies for the core-hole ionized states of CH₄, NH₃, H₂O and HF. To our best knowledge, the experimental data of the geometry changes have not been reported except for CH₄. The bond lengths calculated by the equivalent core model with the CCSD/cc-pVTZ were also shown for comparison. By core-electron ionization, the bond length was predicted to shrink in the case of CH₄ and NH₃ by $\Delta R = -0.053$ and -0.031 Å, respectively, by the SAC-CI calculations. These bond length shrinks were also obtained by the equivalent-core CCSD calculation, but the geometrical changes were evaluated larger. The structure change of NH₃ is characteristic; the bond angle of HNH becomes larger by 6.4° and the structure of NH₃ becomes more flat activating the symmetric stretching and bending vibrations. On the other hand, the bond length of H₂O was predicted to be slightly elongated and the bond length change of HF was estimated as large as $\Delta R = +0.080$ Å. The bond angle of H₂O opens up to about 118° by the O1s ionization. The vibrational spectrum of this state was simulated by calculating the three-dimensional potential energy surface and the theoretical spectrum showed a good agreement with the experiment; namely, the geometry change was accurately calculated¹⁸. It should be noted that the bond angles of the core-hole states of NH₃ and H₂O calculated by the SAC-CI method are slightly different from those obtained by the equivalent core model. The calculated adiabatic energies agree well with the experimental values³⁵; the average deviation was 0.3 eV for these molecules.

Core-Electron Excitation Spectrum of CH₄

Next, the C1s excitation spectrum and excited-state geometries of CH₄ are discussed. The C1s excitation spectrum of CH₄ has been well studied in many experimental^{36–40} and theoretical^{36,38,41} works. Ueda et al.³⁶ reported a high-resolution absorption spectrum and gave reliable assignments with the *ab initio* SCF calculation and detailed analysis of term values. Table III summarized the calculated vertical excitation energy and oscillator strength

with the experimental values. In the present calculation, Rydberg *s*, *p* and *d* excited states of the principal quantum number $n = 3, 4$ and 5 were calculated: transition to the T_2 state is dipole-allowed and those to A_1 and E states are forbidden. Figure 1 compares the calculated SAC-CI spectrum with the XPS experiment³⁶.

TABLE II
Equilibrium geometries of the ground and core-ionized states of CH_4 , NH_3 , H_2O and HF

Molecule	State	Method	R_e , Å	HXH, °	IP, eV
CH_4	ground	SAC	1.090	104.3	–
		Experimental ^a	1.087	104.3	–
	C1s ionized	SAC-CI	1.037	104.3	290.50
		Experimental	1.039 ^b	104.3 ^b	290.86 ^c
	C1s ionized (equivalent core)	CCSD	1.021	104.3	–
NH_3	ground	SAC	1.012	107.0	–
		Experimental ^a	1.014	107.2	–
	N1s ionized	SAC-CI	0.981	113.6	405.15
		Experimental ^c	–	–	405.52
	N1s ionized (equivalent core)	CCSD	0.975	111.3	–
H_2O	ground	SAC	0.957	104.8	–
		Experimental ^a	0.958	104.5	–
	O1s ionized	SAC-CI	0.965	118.2	539.60
		Experimental ^c	–	–	539.82
	O1s ionized (equivalent core)	CCSD	0.960	112.2	–
HF	ground	SAC	0.915	–	–
		Experimental ^a	0.917	–	–
	F1s ionized	SAC-CI	0.995	–	693.89
		Experimental ^c	–	–	693.80
	F1s ionized (equivalent core)	CCSD	0.987	–	–

^a Ref.⁴⁷; ^b ref.²⁹; ^c ref.³⁵

The reliable assignments of this absorption spectrum have been reported³⁶. The present results are in accord with this assignment. From theoretical spectrum without vibrational levels in Fig. 1c, peak 1 is assigned to the forbidden $3s_{a_1}$ state, peaks 3, 9 and 12 to $3pt_2$, $4pt_2$ and $5pt_2$ states, respectively, and peaks 6, 10 and 12 to $3dt_2$, $4dt_2$ and $5dt_2$ states, respectively. The energy separations between these states are in excellent agreement with the experimental values, though the excitation energies are overestimated by 0.3–0.5 eV. The theoretical oscillator strengths of these states reasonably decrease as the principal quantum number becomes large.

TABLE III
Core-electron excited states of CH_4 calculated by the SAC-CI method with [6s5p1d] + Rydberg [5s5p5d]

Peak	Experimental ^a		SAC-CI			Assignment	
	ΔE , eV	relative energy, eV	ΔE , eV	relative energy, eV	f	electronic state	vibrational level
1	287.05	-0.94	287.23	-1.27	0.0000	$3s_{a_1}$	$3s_{a_1} + vib^a$
2	287.40	-0.59					$3s_{a_1} + vib^a$
3	287.99	0.00	288.50	0.00	0.0055	$3pt_2$	
4	288.2–288.3						$3dt_2 + vib^a$
5	288.39	0.40					$3pt_2 + v_1$
6	288.67	0.68	289.19	0.69	0.0025	$3dt_2$	
7	288.85	0.86					$3pt_2 + 2v_1$
8	289.12	1.13					$3dt_2 + v_1$
			289.34	0.84		$4s_{a_1}$	
			289.54	1.04		e	
9	289.43	1.44	289.78	1.28	0.0018	$4pt_2$	
10	289.63	1.64	289.93	1.43	0.0010	$4dt_2$	
11	289.83	1.84					$4pt_2 + 2v_1$
			290.05	1.55		$5s_{a_1}$	
12	289.95	1.96	290.30	1.80	0.0017	$5pt_2$	
			290.35	1.85	0.0003	$5dt_2$	
13	290.22	2.23					
14	290.36	2.37					
15	290.59	2.60					

^a Ref.³⁶

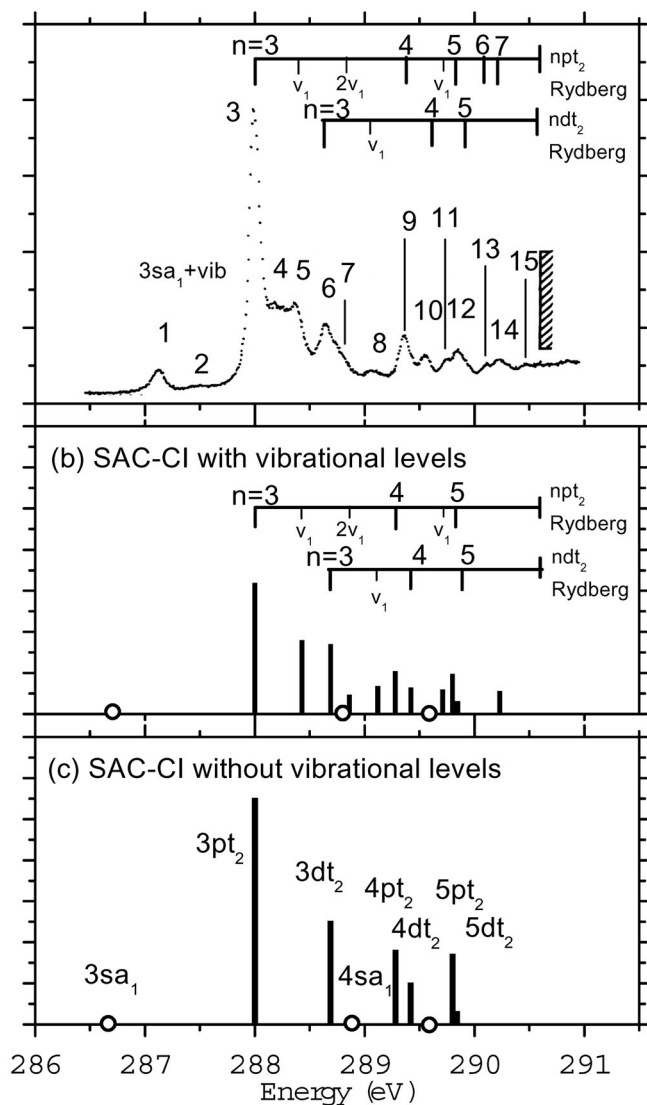


FIG. 1

High resolution electron yield spectrum of C1s excitation spectrum of CH₄ from ref.³⁶ (a). SAC-CI spectrum with (b) and without (c) including vibrational levels of the totally symmetric stretching mode. Theoretical spectrum was shifted by -0.5 eV

Next, we examine the potential energy curves of the dipole allowed T_2 excited states along the totally symmetric stretching mode. Figure 2a shows the potential energy curves and Fig. 2b the oscillator strength along this coordinate. The valence-Rydberg mixing of the $3pt_2$ state has been intensively discussed for this system^{36,38,41}. As can be seen in Fig. 2, the potential energy curves of these states are very smooth and, therefore, do not

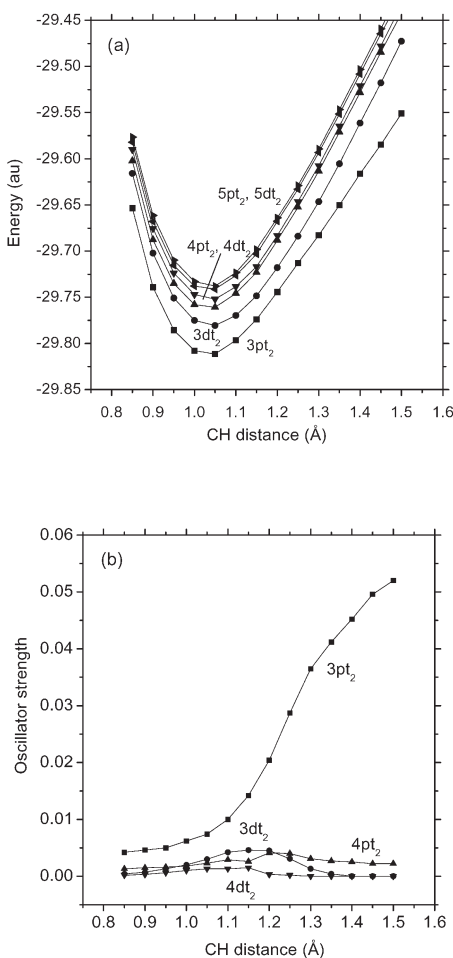


FIG. 2
Potential energy curves (a) and oscillator strength (b) along the totally symmetric stretching mode for the dipole-allowed C1s excited states of CH₄

interact with the valence excitation to the antibonding orbital $2t_2^*$. The oscillator strength also smoothly changes along this coordinate. Therefore, none of these Rydberg excited states interacts with the valence state in this coordinate: these results are in accord with the previous calculation³⁶. The spectroscopic constants of these states are summarized in Table IV. The equilibrium distances of the $3pt_2$ and $3dt_2$ states were calculated to be 1.032 and 1.040 Å; the CH bond shrinks in the same order of the core-ionized state. Note that the ground-state bond distance was calculated to be 1.083 Å with the basis set for calculation of the Rydberg excited states.

The vibrational levels were calculated for the totally symmetric stretching mode. The results of the CH bond length, harmonic frequency, and the Franck–Condon factor ratio were summarized in Table IV. The Franck–Condon ratio of $I(\nu' = 1)/I(\nu' = 0)$ and $I(\nu' = 2)/I(\nu' = 0)$ were calculated to be 0.54 and 0.14 for the $3pt_2$ state, which is in good agreement with the experimental values of 0.58 and 0.11, respectively³⁶. The vibrational spacing was calculated to be 0.43 eV, which is larger than the ground state, 0.39 eV. This is in accord with the experimental observation, but the absolute value was large: the experimental spacing was reported to be 0.39 eV for the $3pt_2$ state. For the $3dt_2$ state, the geometry change is small and, therefore, the Franck–Condon ratio is 0.40 and 0.07 for $I(\nu' = 1)/I(\nu' = 0)$ and $I(\nu' = 2)/I(\nu' = 0)$, respectively. The calculated excitation spectrum including only the totally symmetric vibrational motion is shown in Fig. 1b compared with the experimental spectrum. For the vibrational levels, the present results also support the previous assignment: peaks 5 and 7 are assigned to $\nu' = 1$ and $\nu' = 2$ of the $3pt_2$ state, respectively, for peak 11 $\nu' = 1$ of the $4pt_2$ state, for peak 8 $\nu' = 1$ of the $3dt_2$ state, and for peak 14 $\nu' = 1$ of the $5pt_2$ state.

TABLE IV

Spectroscopic constants and the Franck–Condon factor ratio of the core-electron excited states of CH_4 calculated by the SAC-CI method

State	R_e , Å	ω_e , eV	$I(\nu' = 1)/I(\nu' = 0)$	$I(\nu' = 2)/I(\nu' = 0)$
$3pt_2$	1.032	0.43	0.56	0.14
Experimental ^a		0.39	0.58	0.11
$3dt_2$	1.040	0.43	0.30	0.07
$4pt_2$	1.032	0.43	0.57	0.15
$4dt_2$	1.036	0.43	0.47	0.10

^a Ref.³⁶

Geometry of the Core-Excited States of N_2O and CO_2

The equilibrium structures of the core-excited states of N_2O and CO_2 are characteristic since these molecules have π -electrons. The core-excited Π state of N_2O and CO_2 is doubly degenerate in the linear geometry, but splits into two states along the bending coordinate due to Renner–Teller effect. In the present work, we studied only the lower branch of these split states, i.e., A_1 state of CO_2 and A' state of N_2O .

The structure of the ground state of N_2O was calculated to be $R_{NN} = 1.127 \text{ \AA}$ and $R_{NO} = 1.185 \text{ \AA}$ by the SAC method with the VTZ1P basis sets in comparison with the experimental values of 1.124 and 1.188 \AA , respectively. For N_2O , there are two N1s transitions, i.e., the transitions from the terminal nitrogen N_t^{-1} and central nitrogen N_c^{-1} , the energy separation of these ionized states is ca. 4 eV due to the electronegativity of the adjacent atoms. The N1s- π^* excited states have a bent structure; qualitatively, these states are compared with ONO and NOO molecules in the equivalent core model for N_t and N_c excitations, respectively. The optimized structures of these states are summarized in Fig. 3. For the N_t - π^* excited state, the bond length and bond angle were calculated to be $R_{NN} = 1.192 \text{ \AA}$, $R_{NO} = 1.198 \text{ \AA}$

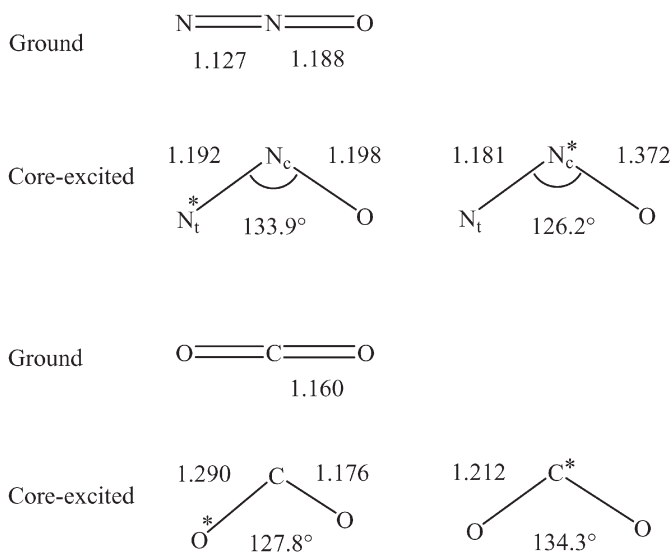


FIG. 3
Calculated equilibrium geometries (in \AA) of the ground and core-electron excited states of N_2O and CO_2

and 133.9° , which shows good agreement with the experimental values of ONO, 1.1945 \AA and 133.9° . The geometry change is more drastic in the N_c excited states: the calculated bond angle of this state was 126.2° and the bond distances were $R_{NN} = 1.181 \text{ \AA}$ and $R_{NO} = 1.372 \text{ \AA}$. The bent structure of the core-excited states was also found in the $O1s-\pi^*$ excited state^{42,43}. The valence-Rydberg coupling changes drastically in this bent coordinate and causes the significant intensity changes of the $O1s$ excited states of N_2O at the high temperature⁴³.

Next, we discuss the structure of the ground and core-excited states of CO_2 . The bond length of the ground state of CO_2 was calculated to be 1.160 \AA in agreement with the experimental value 1.160 \AA . The core-excited states of CO_2 also have bent structures due to the Renner-Teller effect, while the equilibrium structures of core-ionized states are linear. Recently, the vibrational spectrum of the $C1s-\pi^*$ states was intensively studied by XPS and the nuclear motion and geometry of CO_2 in their core-electron excited states were experimentally probed^{44,45}. In the $C1s-\pi^*$ excitation, the bond length and bond angle relax to 1.212 \AA and 134.3° , respectively. Compared with ONO, the equivalent-core molecule, the bond angle is almost the same. Nobusada⁴⁶ studied the potential energy surface of the $C1s-\pi^*$ state of CO_2 using the MRSDCI method and calculated the bond distance and bond angle as 1.217 \AA and 132.9° , respectively, which are in accord with the present values. On the other hand, the stable structure of the $O1s-\pi^*$ excited state of CO_2 is also nonlinear, but asymmetric: the calculated bond lengths of CO^* and CO were 1.290 and 1.176 \AA , respectively, and the bond angle was 127.8° .

CONCLUSIONS

The SAC-CI method has been applied to the geometries of some core-excited and ionized states. The core-hole states of CH_4 , NH_3 , H_2O and HF show characteristic changes: the bond lengths change to -0.05 – $(+0.08) \text{ \AA}$ and bond angles to 6 – 14° . The calculated CH bond length of the $C1s$ ionized state for CH_4 is in good agreement with the simulated result of the experimental spectrum.

The $C1s$ excitation spectrum of CH_4 was calculated and the results show good agreement with the experimental ones. The potential energy curves of T_2 states were calculated for the totally symmetric mode and the vibrational spectrum was simulated. The vibrational structure was well reproduced, which shows that the equilibrium geometries of these excited states were correctly calculated.

The characteristic stable geometries of the core-excited states of N₂O and CO₂ were examined. The structures optimized by calculating the hole state directly agree with the experimental values of the corresponding equivalent core molecules; the π^* excited states have bent structures.

Finally, we would like to state that the Second Japan–Czech–Slovakia Symposium was quite successfully held at the Fukui Institute for Fundamental Chemistry of Kyoto University in December 7–9, 2007. All the attendants enjoyed high-level presentations, active discussions, and a very friendly atmosphere among the three countries. We deeply appreciate *Prof. Rudolf Zahradník* who initiated the idea of having joint symposium of the Czech Republic and Japan together with Prof. Zdeněk Havlas and H. N. in beautiful Villa Lanna in Prague in April 2004. We would like to dedicate this small piece of science to *Prof. Zahradník, on the occasion of his 80th birthday*, for his profound contributions to the development of quantum molecular science and for his leadership in the quantum science community of the world.

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