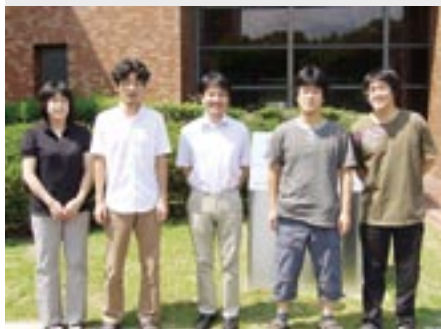


# Theoretical Study on Molecular Excited States and Chemical Reactions

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Molecules in the excited states show characteristic photo-physical properties and reactivity. We investigate the molecular excited states and chemical reactions which are relevant in chemistry, physics, and chemical biology with developing the highly accurate electronic structure theory. We are also interested in the excited-state dynamics and energy relaxation so that we also develop the methodology of large-scale quantum dynamics. In this report, we report our recent studies on the development of the active-space method,<sup>1)</sup> molecular excited states,<sup>2-4)</sup> in particular the inner-shell spectroscopy<sup>3,4)</sup> and catalytic reaction on surface.<sup>5)</sup>

## 1. Development of Active-Space Method<sup>1)</sup>

Radicals show characteristic spectroscopic properties and reactivity in their ground and excited states. Since they are unstable and short-lived, their spectroscopic properties and reactions have to be examined through suitably designed experimental procedures, such as flash photolysis and matrix isolation spectroscopy, to mention a few examples. Excellent experimental techniques using argon and solid parahydrogen matrices have been developed for this purpose. Thanks to these and related advances, a large amount of experimental data has been accumulated for radicals, and a highly accurate theoretical analysis has become an indispensable tool for obtaining a detailed interpretation of these data.

In this work, we have developed the active-space method based on the SAC-CI method and applied the theory to the molecular spectroscopy of open-shell systems. The low-lying valence excited states of four open-shell triatomic molecules, CNC, C<sub>2</sub>N, N<sub>3</sub>, and NCO, were investigated using the electron-attached (EA) and ionized (IP) SAC-CI general-*R* as well as the full and active-space EA and IP EOMCC methods. A comparison was made with experiment and with the results of the completely renormalized (CR) CC calculations with singles, doubles, and non-iterative triples defining the CR-CC (2,3) approach. Adiabatic excitation energies of the calculated states were in reasonable agreement with the experimental values, provided that the 3-particle–2-hole (3p-2h) components

in the electron attaching operator, as in the EA SAC-CI SDT-*R* and EA EOMCCSD(3p-2h) approaches, are included in the calculations for the excited states of C<sub>2</sub>N and CNC which have a predominantly two-electron character. The results also revealed that the active-space EA/IP EOMCC schemes with up to 3p-2h/3h-2p excitations are able to accurately reproduce the results of their much more expensive parent methods while requiring significantly less computational effort. Furthermore, the more “black-box” CR-CC(2,3) approach calculated the lowest state of each symmetry with the same accuracy as that obtained with the EA/IP SAC-CI SDT-*R* and EA/IP EOMCCSD (3p-2h/3h-2p) methods, confirming the significance of higher-order correlation effects in obtaining an accurate description of excited states of radicals, particularly the valence excited states of the CNC and C<sub>2</sub>N species dominated by two-electron processes. Table 1 summarizes the results of the ground and excited states of C<sub>2</sub>N.

**Table 1.** Spectroscopic constants of the ground and excited states of C<sub>2</sub>N.

State	Method	Exc. level	$R_{CC}$ (Å)	$R_{CN}$ (Å)	$T_e$ (eV)
X <sup>2</sup> Π	SD- <i>R</i>	1	1.405	1.191	---
	SDT- <i>R</i> {4,4}	1	1.400	1.185	---
	Expt.		---		---
A <sup>2</sup> Δ	SD- <i>R</i>	2	1.352	1.185	6.004
	SDT- <i>R</i> {4,4}	2	1.315	1.207	2.837
	Expt.		---		2.636
B <sup>2</sup> Σ <sup>-</sup>	SD- <i>R</i>	2	1.354	1.188	7.632
	SDT- <i>R</i> {4,4}	2	1.302	1.223	3.640
	Expt.		---		2.779
C <sup>2</sup> Σ <sup>+</sup>	SD- <i>R</i>	2	1.341	1.192	6.578
	SDT- <i>R</i> {4,4}	2	1.311	1.214	3.594
	Expt.		---		3.306

## 2. Relativistic Effects in *K*-Shell Ionizations: SAC-CI General-*R* Study Based on the DK2 Hamiltonian<sup>3)</sup>

Core-electron binding energies (CEBEs) contain infor-

mation not only about inner-core electrons but also about valence electrons and chemical bonds. Extensive experimental studies have provided the CEBEs of numerous molecules. Siegbahn *et al.* summarized the electron spectroscopy for chemical analysis (ESCA) data in 1969 and Bakke *et al.* reported further ESCA data in 1980. They also clarified the important chemical implications involved in the CEBE data. The recent development of high-resolution soft X-ray photoelectron spectroscopy (XPS) has enabled accurate experimental observations of the CEBEs, resolving the vibrational structure.

It is now generally recognized that the relativistic effect is important in chemistry in particular for the molecular properties of the heavy elements. The methodologies of relativistic quantum chemistry have been developed and established. The relativistic effect is also important in core-electron processes. Although the spin-orbit splitting of the inner-shell P and D states has been intensively investigated, the relativistic effect has not been so much focused in the accurate calculation of the CEBEs for the heavy elements. Most calculations including both electron correlations and relativistic effect have been performed for molecules containing first-row atoms except for the recent work of Barysz and Leszczynski for the rare gas atoms.

In this work, we investigated the relativistic effects in the CEBEs of molecules containing the second-row atoms, Si, P, S, and Cl as well as the F atom. We performed the SAC-CI general-*R* calculations based on the spin-free part of the second-order Douglas-Kroll-Hess (DK2) Hamiltonian.<sup>3)</sup> Table 2 summarizes the results of the relativistic and non-relativistic SAC-CI calculations. The relativistic effect in the CEBEs of the second-row atoms was found to be 4–9 eV. The effect was mostly overestimated by the Koopmans' theorem and was reduced to the extent of 0.15–0.4 eV by including the orbital relaxation and electron correlations.

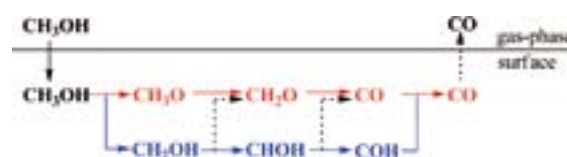
**Table 2.** Calculated and observed Si, P, S, and Cl 1s CEBE (eV).

Mol.	Exptl.	Rel. SAC-CI	Non-Rel. SAC-CI	Rel. effect (eV)	
				SAC-CI	Koopmans'
SiH <sub>4</sub>	1847.1	1848.24	1843.96	4.28	3.97
PH <sub>3</sub>	2150.5	2151.25	2146.32	4.93	5.30
H <sub>2</sub> S	2478.5	2479.51	2472.98	6.53	6.94
OCS	2480.3	2481.84	2475.06	6.78	6.93
CH <sub>3</sub> Cl	2829.4	2832.15	2823.35	8.80	8.95

### 3. Theoretical Study of the Methanol Dehydrogenation Reaction on Pt and Ag Surfaces/Clusters<sup>5)</sup>

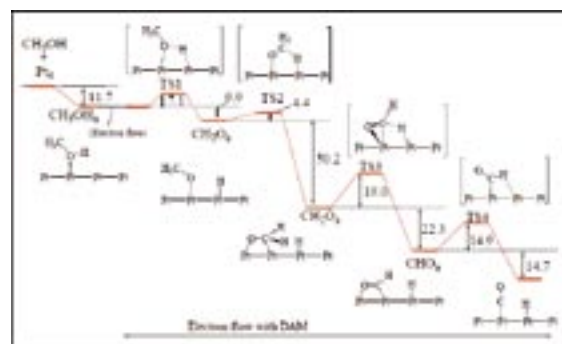
The mechanism of the methanol dehydrogenation reaction on a Pt surface has been investigated using the dipped adcluster model (DAM) combined with density functional theory (DFT) calculations. Reaction pathways starting from CH and OH

dissociations (Figure 1), both of which were proposed experimentally, but, not fully understood, have been examined.



**Figure 1.** Reaction pathways of the dehydrogenation of CH<sub>3</sub>OH to CO.

Starting from O–H bond scission, methanol decomposes to form CO exothermically on the Pt surface, where the Pt-*d* $\sigma$  orbital effectively interacts with the O–H antibonding orbital. The donative interaction of the Pt *d* $\sigma$  orbitals was found to be important for catalytic activation on the Pt surface. Figure 2 shows the overall energy diagram of the methanol dehydrogenation reaction starting from C–H bond scission has a larger activation barrier and, therefore, is less kinetically favorable. Electron transfer from the bulk, which is included in the present DAM calculation, plays an important role in the reaction pathway from O–H bond scission, in particular for the dehydrogenation of formaldehyde. On the other hand, the Ag surface has been shown to be effective for formaldehyde synthesis, because formaldehyde desorbs spontaneously from the Ag surface. The present reaction has also been examined and discussed in view of the nanoscale clusters and nanorods.



**Figure 2.** Overall energy diagram of methanol dehydrogenation starting from OH bond dissociation.

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#### Award

EHARA, Masahiro; APATCC (Asia-Pacific Association of Theoretical & Computational Chemists) 2009 Pople Medal.