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The Effects of One- and Multi-Particle Basis on $^2A_1' \rightarrow {}^2A_2''$ Transition of Al_3

Kyoung-Koo Baeck

Department of Chemistry, Kangnung University, Kangnung 210-702, Korea
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The diversity of electronic structures of metal clusters has been subjected by many experimental and theoretical studies. As one of the simplest member of clusters, aluminum trimer also has several low-lying electronic states, and many experimental works[1~7] have been devoted to characterize these states. In order to make further understandings on these states, reliable theoretical results are required for energetic properties and vibrational properties. In spite of more than fifteen theoretical works treated Al_3 system, only some of them[8~13] are interested on the characterization of the excited states. Though the identity of the ground states, $2A_1'$ in D_{3h} structure, established by ESR and photoelectron experiments[5,7] are supported by an ab *initio* study,[8] there are some disagreements between previous theoretical results on the properties of these states, *i.e.*, the geometries, vibrational properties, the correct order of states, and energetic splittings between them. One of the main reason of these discrepancies stems from the fact that the effect of one- and multi-particle basis size is not explored completely. In constrating to Al_2, where several extensive studies with basis containing f-functions are reported,[14,15] no comparable theoretical study is reported yet for Al_3.

According to previous theoretical studies and experimental results, the adiabatic energetic splittings between these low-lying states are expected to be only a few tenths of eV. The harmonic frequencies range from 150 cm^{-1} to 350 cm^{-1}. In order for a theoretical result to be informative and predictive enough for these closely spacing states, proper choice of one-particle basis set and adequate treatement of electron correlations are indispensible. The main purpose of this work is to report the effects of f-type basis function, the effects of core-correlation, and the effects of triple excitations in electron correlations on the $^2A_1' \rightarrow {}^2A_2''$vibronic transition of Al_3, for which reliable experimental results are reported recently.[6,7]

The potential energy surface of these states are very flat and the electron correlations are treated by the coupled-cluster correlation methods which are highly efficient and size

consistent. The coupled-cluster single and double (CCSD) method[16] and the inclusion of the noniterative triples by the CCSD(T) method[17] are applied to study the effect of the triple excitations on electron correlations. The restricted open-shell Hartree-Fock (ROHF) single reference functions are used mainly because the energy separation from the nearest quartet state, $^4A_2$ in C_{2v} structure, are calculated to be less than 0.3 eV.[8,10]

The TZ2P (12s9p2d)/[6s5p2d] and the TZ2Pf (12s9p2d1f)/[6s5p2d1f] basis, as well as the PVDZ (12s8p1d)/[4s3p1d] and the PVTZ (15s9p2d1f)/[5s4p2d1f] basis of Dunning[18] are used to study the effect of the f-type basis function. The TZ2Pf basis is made by argumenting one f-function (ξ= 0.240) to TZ2P basis, which is made by adding two d-functions (ξ=0.100, 0.315) to McLean-Chandler (12s9p)/[6s5p] basis.[19] Spherical polarization functions (5d,7f) are used through this work.

Because the computation times for high level electron correlation methods are proportional to the high power of the number of active molecular orbitals (MO), much computational requirements can be reduced substantially by freeze just a few portion of MOs.[20] Two, four, and ten core electrons of each Al atom, corresponding 1s,2s,2p-electrons, are frozen during the electron correlations in the drop-MO (3), the drop-MO(6), and the drop-MO(15) methods, respectively. Because of the segmental contraction in TZ2P and TZ2Pf basis, three outermost virtual molecular orbitals (MO) have unreasonably high MO energies, and these three MOs are also frozen during the post-HF calculations of the drop-MO(n) methods with TZ2P and TZ2Pf basis. All electrons and all MOs are participating in the all-MO correlation method. The computation times for the CCSD method, for example, roughly proportional to $N_c^3 \times N_v^3$ where N_c and N_v are the numbers of the occupyed MOs and the virtual MOs, respectively. Only about 5% computation times are required for the drop-MO(15) calculations compare with the corresponding all-MO calculations in this work.

The bond length of the $^2A_1'$ and the $^2A_2''$ states are optimized within D_{3h} structure by the numerical gradient method. Any deviations from the given symmetry results the increase in energy by the present methods. The adiabatic transition energy for $^2A_1' \rightarrow {}^2A_2''$ is calculated by the difference in total energies at their optimized geometries. The force constants for the harmonic frequencies are calculated by the numerical derivation of the first-order energy gradient obtained by the recently developed[21] analytic gradient methods with frozen MOs in the coupled-cluster methods. This analytical gradient method with the dropped MO space is recently implemented in the ACES-II program system.[22] The total energies, bond lengths, symmetric harmonic frequencies, and the vibronic transition energy are calculated with different one- and multi-particle basis, and the results are shown in Table 1.

The difference between the results by the all-MO method and those by the drop-MO method, which will be designated as the '*drop-MO effect*' in this work, corresponds to the core-correlation (core-core and core-valence correlation) effects[23] of the given method with the given basis set. The drop-MO effects of the frozen 1s,2s,2p-electrons by the drop-MO(15) method are about +0.01Å on bond-length and about -100 cm^{-1} on transition energy, except the results with PVTZ basis in which the effects are about 0.02-0.03 Å and ~250 cm^{-1}, respectively. It looks like that the core-correlation effects are exaggerated by the drop-MO methods with the PVTZ basis, partially because the basis functions for the core electrons in the correlation-consistent PVTZ basis are optimized including the electron correlations while this core-correlations are neglected in the drop-MO methods. The drop-MO(6) method reduce the drop-MO effect by half and the results with PVDZ/CCSD and TZ2Pf/CCSD(T) are shown for the comparisons. The drop-MO(3) method produce virtually the same results as those by the all-MO methods. The drop-MO effect on the harmonic frequencies is almost negligible in all cases.

The effects of a f-type function in one-particle basis is reflected in the difference between the results with TZ2P and TZ2Pf basis. The effects turn out to be important in this system, about -0.01 Å on bond-length and +300 cm^{-1} on the transition energy. The effect on the harmonic frequencies is still insignificant, less than +10 cm^{-1}. The same trends and similar magnitudes of the effects of a f-function and the core-correlations were discussed in the previous extensive studies[14] for Al_2.

The effects of the triple electron excitations in correlation methods can be conjectured from the differences between the results of CCSD and those of CCSD(T). While the ef-

Table 1. Results for total energies ($E_{min}=E_{tot}+720$ a.u.), bond lengths R_e(Al-Al), harmonic frequencies $\omega(a_1')$, and the transition energy (T_e) of Al_3

	$E_{min}(^2A_1')$ (a.u.)	R_e(Å)		$\omega(a_1')$(cm^{-1})		T_e(cm^{-1})
		$^2A_1'$	$^2A_2''$	$^2A_1'$	$^2A_2''$	$^2A_1' \rightarrow {}^2A_2''$
PVDZ/CCSD						
All-MO	−5.876670	2.5837	2.6821	341	296	1002
Drop-MO(6)	−5.874314	2.5865	2.6856	339	295	977
Drop-Mo(15)	−5.861945	2.5944	2.6945	336	293	892
PVDZ/CCSD(T)						
All-MO	−5.894746	2.5783	2.6695	348	306	1472
Drop-M0(15)	−5.879363	2.5898	2.6820	343	302	1370
TZ2P/CCSD						
All-MO	−6.248727	2.5540	2.6558	337	292	978
Drop-MO(15)	−5.872813	2.5560	2.670	338	293	904
TZ2P/CCSD(T)						
All-MO	−6.271462	2.5457	2.6402	346	303	1521
Drop-MO(15)	−5.892456	2.5484	2.614	348	305	1480
PVTZ/CCSD						
All-MO	−6.101282	2.5257	2.6228	360	314	1334
Drop-MO(15)	−5.903745	2.5504	2.6511	348	304	1066
PVTZ/CCSD(T)						
All-MO	−6.127512	2.5201	2.6099	368	326	1858
Drop-MO(15)	−5.925804	2.5441	2.6363	358	316	1630
TZ2Pf/CCSD						
All-MO	−6.127512	2.5201	2.6099	352	307	1301
Drop-MO(15)	−5.888867	2.5470	2.6452	350	306	1199
TZ2Pf/CCSD(T)						
All-MO	−6.291817	2.5342	2.6256	362	319	1832
Drop-MO(6)	−6.147974	2.5381	2.6298	361	318	1804
Drop-MO(15)	−5.911090	2.5407	2.6317	360	318	1760

Table 2. Some theoretical and experimental data for $^2A_1'$ and $^2A_2''$ states of Al_3

Basis set/Method	R_e(Al-Al) (Å)		$^2A_1'$ (ω, cm^{-1})		$^2A_1'$ (ω, cm^{-1})		T_e cm^{-1}	Ref
	$^2A_1'$	$^2A_2''$	a_1'	e'	a_1'	e'		
ECP+(DZ+P)/CASSCF	2.569	2.663					1802	8
ECP+(3s3p1d)/SCF-CCI	2.593	2.863					887	9
ECP+3s3p1d)/MRD-CI	2.553	2.693	285	199	261		− 565	10
ECP+(3s3p1d)/GVB-CI	2.620							11
(6s4p1d)/CCx+ST4	2.602		289					12
(5s4p2d)/MCSCF	2.570	2.66					1207	13
(6s5p2d1f)/Drop-MO(15)								
CCSD(T)	2.541	2.632	360	236	318	188	1760	This
CCSDT[a]							1533	work
IR-Spectrum				245	319		1770	6
Photo-electron			360	235	315	195	1550	7

[a] E_{tot} ($^2A_1'$)= − 725.912151 a.u.

fect of the triple excitations on bond-length is about − 0.01 Å, which probably can be neglected, the effect on the transition energy is about +500 cm^{-1} which is definitely not small for a predictive studies on these closely spacing states. This results explain why previous thoeretical studies in Table 2 without triple excitation produced an unproper values for the excitation energy. The effect of the triple excitations also can be considered from a multi-reference character of these electronic states. Relatively correct results[8] by the CASSCF method implys the multi-reference character of the $^2A_2''$ state. It is now well established that the inclusion of the noniterative triple excitation is an efficient method to minimize deficiencies caused by the multi-reference character. The effect on the harmonic frequencies, however, is still less than 10 cm^{-1}, which can be neglected in most cases.

Considering these three effects together, the effects of the core-correlations probably can be neglected without significant deterioration in the quality of results provided by the proper choice of basis for core-electrons, while the effects of a f-type function in one-particle basis and the effects of the triple excitations in multi-particle basis can not be neglected for a predictive results. The efficient and reliable combination of one- and multi-particle basis for the study of low-lying electronic states of Al_3 is the combination of the CCSD(T) correlation method, a basis set containing at least one f-type function, and the exclusion of the 1s,2s,2p-electron correlations which requires computational times only 5% of all-MO method.

When the effect of the zero-point vibrational energy (ZPE), calculated from experimental or theoretical harmonic frequencies, is included, the transition energy decrease about 70 cm^{-1}. On the other hand, the transition energy increase about 70-90 cm^{-1} by the inclusion of the core-correlations. As a result, the result of the drop-MO(15) method without ZPE correction can be compared with experimental value directly in this case.

In order to estimate the qualities of results with the present method, the drop-MO(15)/CCSD(T)/TZ2Pf method, the adiabatic transition energy at the geometries optimized with drop-MO(15)/CCSD(T) method is calculated again by the drop-MO(15) method with the CCSDT[24] coupled-cluster theory which includs full triple excitations in electron correlations. The results are given in Table 2 along with other previous theoretical results and recent experimental results. The vibrational frequencies and the transition energy by the present work are much closer to experimental values than other previous results, and the bond lengths of this work, which is shorter than any other previous value, is expected to be the most reliable one among ever suggested values. Even though a good agreements between experimental harmonic frequencies and the theoretical results with CCSD(T)/TZ2Pf method are already well established for usual organic molecules,[25] the perfect agreements between experimental values and the present results for the harmonic frequencies of these two states are quite encouraging for futher applications of this method. The results of this work will be utilized in studying all possible vibronic transitions between low-lying electronic states of Al_3. At least six states are belived to be detected experimentally.[4,7]

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A Practical Procedure for the Preparation of (1*E*,3*E*)-5-Alkoxy-1-siloxy-1,3-dienes

Sun Ho Jung*, Mun Su Yeo, Soon Ok Kim, and Chan Seong Cheong†

Department of Chemistry, Sungshin Women's University, Seoul 136-742, Korea
†Division of Applied Science, Korea Institute of Science and Technology, Seoul 136-791, Korea
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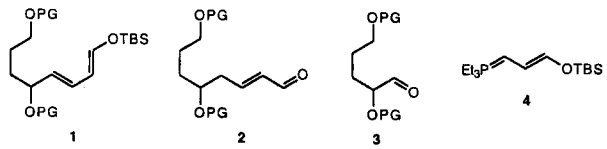
Siloxydienes have been widely used in organic synthesis. They are known to take a variety of electrophiles in the presence of Lewis acid or fluoride anion.[1] They are also finding widespread use in Diels-Alder reactions.[2] During studies related with substituent effects on the stereo- and regiochemical outcome of Diels-Alder reaction, we needed to prepare various (1*E*,3*E*)-5-alkoxy-1-siloxy-1,3-dienes such as **1**. Generally, 1-siloxy-1,3-dienes have been prepared from α,β-unsaturated aldehydes by deprotonation of the γ-position followed by trapping of the resulting anions with the silylating agents.[1d,2c] Unfortunately, these methods do not work well with δ-alkoxy-α,β-unsaturated aldehydes such as **2**.[3] Elimination of the δ-alkoxy group is known to be a serious obstacle to access to desired dienes. Such difficulties can be removed by employing the Wittig process, for example, by reacting α-alkoxyaldehydes **3** with phosphoranes **4**.[3,4] However, the stereoselectivities which attend such procedure are not satisfactory (ratios of 1*E*,3*E*-dienes to other dienes are ~2 : 1). Thus, the development of a more practical and stereoselective procedure for the preparation of (1*E*,3*E*)-5-alkoxy-1-siloxy-1,3-dienes is of value.



We have examined the preparation of (1*E*,3*E*)-5-alkoxy-1-siloxy-1,3-dienes from δ-alkoxy-α,β-unsaturated aldehydes, in hopes that achievement of simultaneous deprotonation and enolate trapping could minimize the elimination of the δ-alkoxy group. It was also anticipated that at low temperatures, kinetic deprotonation would occur with maintenance of the initially preferred transoid relationship between the C=O group[5] and the C=C bond to secure the *E*-stereochemistry of the siloxy-containing double bond.

Upon surveying reaction conditions using δ-*t*-butyldimethylsilyloxy-α,β-unsaturated aldehyde **5a** as a model substrate, it was found that treatment of the enal **5a** with lithium bis(trimethylsilyl)amide in the presence of *t*-butyldimethylsilyl chloride in tetrahydrofuran-hexane containing hexamethylphosphoramide (~5 : 1 THF-Hexane/HMPA) at