Linkage Isomerism and the Relativistic Effect in Interaction of Lanthanoid and Carbon Monoxide

Gongyi Hong, Xianjie Lin, Lemin Li,* and Guangxian Xu

State Key Laboratory of Rare Earth Materials and Applications, Department of Chemistry, Peking University, Beijing 100871, China

Received: February 26, 1997; In Final Form: June 27, 1997[⊗]

The interaction between La, Gd, or Lu atoms and carbon monoxide has been studied by means of the density functional method with gradient correction and quasi-relativistic correction. Three linkage isomers, Ln−CO (I), Ln−OC (II), and Ln−(η^2-CO) (III) have been obtained through full geometric optimization. The vibrational frequencies and the dissociation energies (D_e) for decomposition into Ln atoms and CO have been calculated. The calculated frequency related to the C−O bond (ν_{C-O}) of Gd−CO is in good agreement with the experimental value. The ordering of the dissociation energy is D_e(La) > D_e(Gd) > D_e(Lu) for the same isomer with different lanthanoid atom, and it is D_e(I) > D_e(III) > D_e(II) for different isomers with the same lanthanoid. However, isomer III has much lower ν_{C-O} than does isomer I, showing that the traditional assumption used to estimate the binding strength between the metal and CO by the lowering of ν_{C-O} is not always valid. For La−CO and Gd−CO, the relativistic effect produces little changes in the calculated bond lengths and vibrational frequencies, but it significantly reduces the dissociation energy. For Lu−CO the relativistic effect lowers the spin multiplicity of the molecule in the ground state, significantly enlarges the bond lengths between Lu and CO, reduces the dissociation energy, and raises the ν_{C-O}. It is found that the bond formation can be described as the donation of the CO 5σ electrons to the Ln 5dσ orbitals in synergy with a feedback of the Ln 5dπ electrons to the CO 2π* orbitals. For isomer II the CO 5σ donation is very weak, and for isomer III both the CO 5σ and 1π electrons participate in donation. The donation of the bonding CO 1π electrons to Ln 5d orbitals may be the major cause for the large lowering of ν_{C-O} of isomer III. Accompanying the bond formation, there is transfer of roughly one electron from Ln 6s to 5d orbitals. With the increase of the Ln atomic number, the energy gap between the Ln 6s and 5d levels enlarges rapidly, leading to decrease of the bonding energy for the heavier lanthanoid−carbon monoxide compounds. The relativistic effect lowers the 6s level and raises the 5d level and thus enhances this trend.

1. Introduction

Lanthanoid chemistry has been a fascinating area of research for both theoretical and experimental chemists in recent years. Thousands of new lanthanoid compounds and functional materials have been synthesized and characterized.[1,2] It has been found that some lanthanoid compounds, like some transition metal (TM) compounds, can catalyze the oxidation of carbon monoxide. There have been many experimental and theoretical studies on transitional metal carbonyl compounds. Up to now no macro quantity of lanthanoid carbonyl compounds has been prepared, although some IR spectroscopic studies on matrix isolated lanthanoid carbonyls have been reported.[3,4] No structural data were forthcoming from these studies. First-principle theoretical studies on lanthanoid compounds are also poor, because the relativistic effect is important for lanthanoids and because it is difficult to take into account the correlation effect rigorously.[5−8] The studies on the transition metal carbonyls have shown that the carbon monoxide always coordinates to the TM atoms with the carbon end, and the bonding can be satisfactorily described as the donation of the CO σ electrons to the TM atomic orbitals and the synergetic feedback of the TM ndπ electrons to the CO 2π* orbitals. The lanthanoids have very strong affinity to oxygen and are poor in d electrons. Thus it is of interest to investigate whether the coordination structure and the bonding mechanism of the Ln + CO systems are similar to those of the TM + CO systems. The influence of the relativistic effect on the molecular properties is also of interest. In a previous paper, the linkage isomerism of the lanthanum + carbon monoxide system has been investigated by nonrelativistic density functional calculations without gradient correction.[9] In the present investigation, more systematic studies on the interaction of lanthanoid and carbon monoxide have been performed by means of the density functional theory method with relativistic effect and gradient corrections. La, Gd, and Lu were taken as the representatives of the lanthanoids in the studies. The optimized geometries, vibrational frequencies, and the dissociation energies of different isomers were calculated. The magnitude and sign of relativistic effects and of the gradient corrections were exhausted from the calculated results. The bonding mechanism was investigated by means of a Mulliken population analysis.

2. Computational Details

The calculations were carried out by using the density functional package ADF, release 2.0.1 and 2.2, developed by Baerends et al.[10,11] Local density approximation (LDA) with VWN correlation potential[12,13] and the gradient correction (GRD) for the exchange energy due to Becke[14] and for the correlation energy due to Perdew[15] were adopted. The relativistic effect was taken into account by the quasi-relativistic approach (QR).[16] The basis sets supplied by the ADF program package were used. Double-ζ basis sets were taken for the 2s and 2p orbitals of the carbon and oxygen atoms augmented with an extra 3d polarization function. Triple-ζ STOs were adopted for 4f, 5d, 6s, and 6p orbitals of lanthanoid atoms. It has been found that the 5g polarization functions for lanthanoids are unimportant.[17] Our preliminary calculation supported this

---

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1997.

TABLE 1: Bond Lengths (R_e, in Å), Vibrational Frequencies[a] (ν, in cm^{-1}), and Dissociation Energies (D_e, in eV) of Ln−CO

molecules	schemes	multiplicity	R_e(Ln−C)	R_e(C−O)	ν_1	ν_2	ν_3	D_e
La−CO	LDA	4	2.351	1.167	285	267	1844	2.52
		2	2.274	1.187				2.03
	LDA + QR	4	2.348	1.170	293	272	1826	1.91
		2	2.332	1.174				1.61
	LDA + QR + GRD	4	2.392	1.177	279	268	1778	1.62
		2	2.331	1.181				1.34
Gd−CO	LDA	11	2.249	1.170	334	310	1802	2.36
		9	2.264	1.169				1.69
	LDA + QR	11	2.234	1.171	339	321	1796	1.68
		9	2.232	1.174				1.00
	LDA + QR + GRD	11	2.267	1.179	332	235	1816[b]	1.36
		9	2.269	1.180				0.74
Lu−CO	LDA	4	2.181	1.177	364	300	1842	1.55
		2	2.243	1.166				1.29
	LDA + QR	2	2.338	1.161	264	166	1939	1.17
		4	2.132	1.185				0.74
	LDA + QR + GRD	2	2.423	1.170	225	136	1892	0.92
		4	2.171	1.194				0.39

[a] ν_1, ν_3 refer to the bond stretching vibration modes, and ν_2 refers to the degenerate angular vibration mode. [b] The experimental value is 1840 cm^{-1}.[4]

conclusion, and these functions were therefore neglected in the present investigation. The frozen-core approximation was taken for the inner-core shells. All the geometrical optimization and frequency calculations were carried out by means of the analytical energy gradient method[18,19] in three schemes: LDA,[20] including QR correction (LDA + QR), and further plus nonlocal correction (LDA + QR + GRD),[21] respectively. The dissociation energies were calculated within the spin-unrestricted density functional theory in all the three schemes. They were determined as the total energy differences between the molecules and their dissociation products, all of which are in ground states. Spin multiplicities of 2 and 4 were considered for the lanthanum and lutetium compounds, and 9 and 11 for the gadolinium compounds. The experimental electronic configurations, $4f^x5d^16s^2$ ($x = 0$ for La, 7 for Gd, and 14 for Lu), were assumed in calculations of the metal atomic energies. The contribution of spin−orbit interaction was neglected, considering the fact that it is small for Ln 5d orbitals, while the molecules studied in the present paper have empty, half-occupied or fully occupied 4f subshells.[17,22]

3. Results and Discussion

3.1. Molecular and Electronic Structure of Lanthanoid Carbonyls: Ln−CO. The calculated results show that carbon monoxide preferentially coordinates to the lanthanoid atom with C end to form linear metal carbonyl compounds. In Table 1 presented are the full optimized geometries and the calculated Ln−CO bond dissociation energies of lanthanoid carbonyls in ground states and the first excited states in the three schemes. The vibrational frequencies are also presented for the ground states.

The following points can be seen from Table 1. (1) The spin multiplicity of the molecules in ground states is 4 and 11 for La−CO and Gd−CO, respectively. For Lu−CO, while it is 4 in LDA scheme, it becomes 2 when the relativistic effect is taken into account. (2) While the relativistic effect only slightly influences the bond lengths and vibrational frequencies of La−CO and Gd−CO, it considerably reduces the dissociation energy, by 0.61 eV for La−CO and 0.68 eV for Gd−CO. As for Lu−CO, the relativistic effect exhibits more prominently. Besides lowering the spin multiplicity of the molecule in ground states, it reduces the dissociation energy by 0.38 eV and enlarges ν_{C-O} by 97 cm^{-1} and Lu−C bond length by 0.15 Å. (3) The gradient correction reduces the dissociation energies by about 0.3 eV and enlarges the bond lengths a little. The result is similar to that from previous DFT calculations. (4) The calculated ν_{C-O} of Gd−CO is in good agreement with the experimental one. (5) In the LDA + QR + GRD scheme, that is, after the relativistic effect and the gradient correction are taken into account, the calculated dissociation energies of the molecules in ground states lie in the range of 0.92−1.34 eV, approaching those of transition metal carbonyl compounds. Thus the lanthanoid carbonyls are stable compounds. The dissociation energies decrease with increasing lanthanoid atomic number.

The 4f-like MO's are always empty (La−CO), half-occupied (Gd−CO), or fully occupied (Lu−CO), while the electronic configuration for the three outermost valence electrons is $\sigma^{\uparrow}\pi^{\uparrow\uparrow}$ (higher spin) for Ln−CO, $\sigma^{\uparrow\downarrow}\pi^{\uparrow}$(lower spin) for Lu−CO and $\sigma^{\downarrow}\pi^{\uparrow\uparrow}$(lower spin) for La−CO and Gd−CO. The result of Mulliken population analysis of Ln−CO in ground states is presented in Table 2. The CO molecular orbitals and Ln atomic orbitals were taken as the basis sets for the population analysis. Some information about bonding can be obtained from Table 2. (1) The populations on Ln 4f and 6p orbitals are very close to those of the free atoms. Thus it can be inferred that the Ln 4f and 6p orbitals only slightly participate in bonding. (2) There is strong mixing between CO 5σ and Ln 5dσ orbitals as well as between CO 2π* and Ln 5dπ orbitals. About 0.4 of an electron transfers from CO 5σ to Ln 5dσ orbitals and half to one electron occupies CO 2π* orbitals. This is similar to the case of transition metal carbonyls. Thus the bonding mechanism can be described as the donation of the CO 5σ electrons to Ln 5dσ orbitals in synergy with the feedback of Ln 5dπ electrons to CO 2π* orbitals. (3) It is interesting to note that, for La−CO and Gd−CO, even in lower spin multiplicity, there are still in total about two electrons on Ln 5dπ and CO 2π* orbitals, whereas for Lu−CO, there is only about one electron in those orbitals. Since the mixing of Ln 5dπ and CO 2π* orbitals plays the main role in bonding, this fact can be correlated to the increment of ν_{C-O} and the Lu−C bond length of Lu−CO in the ground state with lower spin multiplicity.

It can be seen from Table 2 that there is about one electron in the Ln 6s orbital and in total about two electrons in Ln 5d and CO 2π* orbitals. Therefore, bond formation involves transfer of about one electron from Ln 6s to 5d orbitals, and a part of the 5d orbital population is shifted to CO 2π* orbitals. This transfer requires promotion energy. The promotion energy increases rapidly with increasing of atomic number of the lanthanoids, which brings about a decrease of the dissociation energy of Ln−CO bonds. It is well-known that the relativistic

TABLE 2: Mulliken Population Analysis of Ln−CO

		CO				Ln				
molecules	schemes	4σ	5σ	1π	$2\pi^*$	4f	$5d\sigma$	$5d\pi$	6s	6p
La−CO	LDA	2.00	1.60	4.00	0.72	0.03	0.47	1.27	0.85	0.03
	LDA + QR	2.00	1.60	4.00	0.76	0.04	0.43	1.22	0.89	0.04
	LDA + QR + GRD	2.00	1.66	4.00	0.76	0.03	0.36	1.22	0.87	0.04
	LDA + QR + GRD[a]	2.00	1.62	4.00	0.58	0.02	0.46	1.42	0.85	0.04
Gd−CO	LDA	2.00	1.60	4.00	0.97	7.06	0.36	0.97	0.86	0.04
	LDA + QR	2.00	1.64	4.00	1.00	7.01	0.35	1.00	0.88	0.05
	LDA + QR + GRD	1.98	1.66	4.00	1.04	6.99	0.30	0.96	0.87	0.06
	LDA + QR + GRD[a]	2.00	1.64	4.00	0.56	7.02	0.47	1.42	0.84	0.04
Lu−CO	LDA	2.00	1.60	4.00	0.82	14.00	0.38	1.17	0.90	0.06
	LDA + QR	2.00	1.72	4.00	0.49	14.00	0.40	0.50	1.72	0.10
	LDA + QR + GRD	1.98	1.76	4.00	0.47	14.00	0.34	0.52	1.72	0.10

[a] In lower spin multiplicity (2 for La−CO and 9 for Gd−CO).

TABLE 3: Bonding Energy Analysis for Ln−CO (in eV)

molecules	E_{steric}	$-E(\sigma)$	$-E(\pi)$	$-E(\delta)$	$-E(\phi)$	E_{prep}	D_e
La−CO	1.41	1.00	2.13	0.00	0.00	0.10	1.62
Gd−CO	1.77	1.22	2.37	0.01	0.01	0.48	1.36
Lu−CO	1.56	1.10	1.44	0.00	0.00	0.07	0.92

TABLE 4: Bond Lengths (Å), Dissociation Energies (eV), and Vibrational Frequencies[a] (cm^{-1}) of Ln−OC

molecules	multiplicity	R_e(Ln−O)	R_e(C−O)	ν_1	ν_2	ν_3	D_e
La−OC	4	2.479	1.178	213	199	1691	0.47
	2	2.564	1.169				0.19
Gd−OC	11	2.328	1.187	219	137	1632	0.11
	9	2.401	1.178				0.04
Lu−OC	2	2.358	1.190	134	129	1628	0.20
	4	2.167	1.215				−1.08

[a] See the note under Table 1.

effect lowers the 6s orbital energy and raises the energy of the 5d orbitals. Thus it enlarges the energy gap between the Ln 6s and 5d levels and the promotion energy for transferring the Ln 6s electrons to Ln 5d orbitals. Although raising Ln 5d level is favorable to the interaction between Ln 5d and CO $2\pi^*$ orbitals, it does not compensate for the increase in the promotion energy. Thus the relativistic effect enhances the downward trend of the dissociation energies of the Ln−CO bonds. For Lu, the relativistic enhancement of the energy gap is so large that 6s to 5d promotion does not take place in bond formation. A consequence of this effect is lower spin multiplicity of the Lu−CO ground state. It is interesting to note that the relativistic effect strengthens the TM−CO bonds of transition metal carbonyls.[23] In that case the predominant factor for TM−CO bonding is the feedback of the TM *n*d electrons to CO $2\pi^*$ orbitals, and the relativistic effect is favorable to this interaction.

The relative contributions of the σ donation and the π feedback is interesting. They may be elucidated by means of the extended transition state method,[24−26] in which the bonding energy is decomposed as follows

$$D_e = -(E_{\text{steric}} + E_{\text{orb}} + E_{\text{prep}})$$

where E_{steric} represents the steric interaction energy between the interacting fragments, lanthanoid atom and CO in this case. This energy includes the Coulombic interaction and so-called Pauli repulsion, which is directly related to the two-orbital three or four electron interaction between occupied orbitals on both fragments. The term E_{orb} originates from the attractive interactions between occupied and virtual fragment orbitals on the two fragments. This term can further be decomposed into contributions from different symmetry components, which are σ, π, δ, ϕ for the present systems. The last term E_{prep} is the preparation energy required to relax the interacting fragments to their ground states, because in their interacting states, the fragments may have geometries and/or electronic configurations that differ from those in their ground states. The calculated results in the LDA + QR + GRD scheme are listed in Table 3.

It can be seen from Table 3 that the π feedback contributes about twice as much as the σ donation to the bonding energy for La−CO and Gd−CO. For Lu−CO these contributions are nearly equal, which is obviously due to the fact that there is only one 5d electron to participate in feedback.

3.2. Linkage Isomerism of Lanthanoid−Carbon Monoxide Compounds. *3.2.1. Structure of Isomer II: Ln−OC.* The full geometric optimization of the Ln + CO systems with the QR + LDA + GRD scheme shows that, besides the lanthanoid carbonyls, CO coordinating to Ln with the O end also gives linear stable configurations, Ln−OC. The equilibrium bond lengths and dissociation energies of Ln−OC bonds of these isomers in ground states and in their first excited states are presented in Table 4. The vibrational frequencies are also reported for the ground states. The three real vibrational frequencies show that the energy extrema correspond to stable configurations rather than to saddle points. The bonding in the isomers Ln−OC is much weaker than that in the isomers Ln−CO, although the lanthanoids usually have very strong affinity to oxygen. The dissociation energies of Ln−OC bonds lie in the range of 0.1−0.5 eV, close to those of hydrogen bonds. On the other hand, the $\nu_{\text{C−O}}$ of Ln−OC is obviously lower than that of Ln−CO, by 87 cm^{-1} for La−OC, 184 cm^{-1} for Gd−OC, and 64 cm^{-1} for Lu−OC. Therefore, the assumption that stronger binding between the metal and CO lowers $\nu_{\text{C−O}}$ more is incorrect in this case. A similar result for TM carbonyls has been found by S.-C. Chung et al.[27] The result of Mulliken population analysis shows that there is strong interaction between Ln $5d\pi$ and CO $2\pi^*$ orbitals, while both CO 4σ and 5σ only weakly interact with Ln $5d\sigma$ orbitals. Thus the feedback of Ln 5d electrons to CO 2 π^* plays the predominant role in bond formation of Ln−OC.

3.2.2. Structure of Isomer III: Ln−(η^2-CO). The full geometric optimization of Ln + CO systems with the LDA + QR + GRD scheme shows that CO and Ln also form stable nonlinear isomers. The equilibrium bond lengths and dissociation energies of these isomers in their ground states and in their first excited states are presented in Table 5. The vibrational frequencies are also reported for the ground states.

The isomers have approximately isosceles triangle configurations. The bonding in Ln−(η^2-CO) is weaker than that in Ln−CO but stronger than that in Ln−OC for all lanthanoids. The heavier lanthanoid forms a weaker bond with CO. It is interesting to note that $\nu_{\text{C−O}}$ of Ln−(η^2-CO) is much lower than that of Ln-CO. With the exception of Lu−(η^2-(CO), for which $\nu_{\text{C−O}}$ is about the same as that of Lu−OC, the $\nu_{\text{C−O}}$ of Ln−(η^2-CO) is also much smaller than that of Ln−OC. Clearly,

TABLE 5: Bond Lengths (Å), Dissociation Energy (eV), and Vibrational Frequencies[a] ($\mathrm{cm^{-1}}$) of Ln−(η^2-CO)

molecules	multiplicity	R_e(Ln−C)	R_e(Ln−O)	R_e(C−O)	ν_1	ν_2	ν_3	D_e
La(CO)	4	2.491	2.500	1.224	371	139	1464	1.01
	2	2.428	2.558	1.225				0.76
Gd(CO)	11	2.358	2.382	1.233	364	247	1477	0.72
	9	2.630	2.538	1.192				0.40
Lu(CO)	2	2.594	2.491	1.200	257	155	1680	0.64
	4	2.217	2.249	1.262				−0.02

[a] ν_1, ν_3 refer to the bond stretching vibration modes, and ν_2 refers to the angular vibration mode.

the C−O bond can be considerably weakened through sideways coordination to Ln. The result of Mulliken analysis shows that there is strong interaction between Ln 5dπ and CO 2π* as well as between Ln 5dσ and CO 5σ orbitals. It should be noted that CO 1π electrons participate in donation to a certain extent, which may be the main reason for the significant decrease of $\nu_{\mathrm{C-O}}$ for Ln−(η^2-CO).

The stability of the isomers to interconversion was examined in the case of Lu + CO. The barriers (in eV) between the three isomers are as follows:

$$\mathrm{Lu{-}CO} \underset{0.17}{\overset{0.45}{\rightleftarrows}} \mathrm{Lu{-}}(\eta^2\text{-CO}) \underset{0.13}{\overset{0.57}{\rightleftarrows}} \mathrm{Lu{-}OC}$$

Thus the three isomers would have stable conformations at lower temperature. Lu + CO isomers are the most weakly bound of the isomers here studied, apart from Gd−OC. Hence, it can be inferred that all isomers studied in the present paper are stable, at least at lower temperatures.

4. Summary and Conclusion

From this investigation of the lanthanoid + carbon monoxide systems by means of the density functional method with gradient and relativistic effect corrections, the following conclusion can be drawn.

(1) The lanthanoid atoms can combine with carbon monoxide to form three isomers in which CO coordinates to Ln with the carbon end (I, Ln−CO), with the oxygen end (II, Ln−OC), and in a side manner (III, Ln−(η^2-CO)). The stability of the isomers is in the order I > III > II, but the vibrational frequency of the C−O bond ($\nu_{\mathrm{C-O}}$) is in the order I > II > III. The $\nu_{\mathrm{C-O}}$ of isomer III has a much lower value. This fact shows that the binding strength between the metal and CO does not always correlate with the lowering of $\nu_{\mathrm{C-O}}$. The nature of the bonding between the metal and CO influences the $\nu_{\mathrm{C-O}}$ significantly.

(2) The calculated vibrational frequency $\nu_{\mathrm{C-O}}$ of Gd−CO is in good agreement with experiment. The calculated dissociation energies of the lanthanoid carbonyls (isomer I) show that the stability of Ln−CO is comparable with that of transition metal carbonyls. The dissociation energies decrease with increasing lanthanoid atomic number for all three isomers. The gradient correction decreases the dissociation energies and increases the bond lengths between Ln and CO.

(3) The relativistic effect only slightly influences the bond lengths and vibrational frequencies but significantly reduces the dissociation energies for La−CO and Gd−CO. For Lu−CO the relativistic effect is more prominent. It lowers the spin multiplicity of the ground states, reduces the dissociation energy, increases the Lu−C bond length, and increases the frequency of the C−O stretching vibration. Thus the relativistic effect must be taken into account in studies of heavier lanthanoid compounds.

(4) The bonding between the lanthanoid and CO can be described as due to σ donation and synergetic π feedback, similar to the case of transition metal carbonyls. However, for isomer II the σ donation is very weak. For isomer III, both the CO 5σ and the CO 1π electrons participate in donation, which may be the main reason for the significant lowering of $\nu_{\mathrm{C-O}}$.

(5) In the bond formation between the Ln atom and CO, about one electron is promoted from the Ln 6s to the 5d orbitals, which requires energy. Although the radius of the lanthanoid atoms decreases with increasing of the atomic number and the interaction between the Ln atom and CO becomes stronger, this increase cannot compensate for the increase of the promotion energy. Therefore, the bonding energy decreases. The relativistic effect lowers the energy of the Ln 6s orbital and raises the energy of the 5d orbitals, thus enhancing the downward trend of the bonding energies.

Acknowledgment. The authors give great thanks to Professor Tom Ziegler for his helpful discussion about DFT method and the use of the ADF program package. This work has been supported by the National Natural Science Foundation of China, which the authors gratefully acknowledge.

References and Notes

(1) Alexander, V. *Chem. Rev.* **1995**, *95*, 273 and references therein.

(2) Schumann, H. M.; Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865 and references therein.

(3) Slater, J. L.; Devore, T. C.; Calder, V. *Inorg. Chem.* **1973**, *12*, 1918.

(4) Sheline, R. K.; Slater, J. L. *Angew. Chem., Int. Ed. Engl.* **1975**, *4*, 309.

(5) Veillard, A., Ed. *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry*; NATO ASI series C176; Reidel: Dordrecht, 1986.

(6) Malli, G. L., Ed. *Relativistic and Electron Correlation Effects in Molecules and Solids*; NATO ASI Series; Plenum: New York, 1993.

(7) Salahub, D. R., Zerner, M. C., Eds. *The Challenge of d and f Elements*: *Theory and Computation*; ACS Symposium Series 394; American Chemical Society: Washington, DC, 1989.

(8) Pyykko, P. *Chem. Rev.* **1988**, *88*, 563.

(9) Hong, G.-Y.; Li, L.-M.; Xu, G.-X.; Lin, X.-J. *Physicochim. Sin. Acta* **1995**, *11*, 481.

(10) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.

(11) ADF program package, Theoretical Chemistry, Vrije Universiteit: Amsterdam, The Netherlands, 1996.

(12) Vosko, S. J.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(13) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(14) Becke, A.D. *Phys. Rev. A* **1988**, *38*, 3098.

(15) Perdew, J. P. Phys. Rev. B, **1986**, *33*, 8822. Erratum, *ibid.* **1986**, *34*, 7406.

(16) Ziegler, T.; Tschinke, V.; Baerends, E. J.; Snijders, J. G.; Ravenek, W. *J. Phys. Chem.* **1989**, *93*, 3050.

(17) Wang, S. G.; Schwarz, W. H. E. *J. Phys. Chem.* **1995**, *99*, 11687.

(18) Fan, L.; Ziegler, T. *J. Chem. Phys.* **1992,** *96*, 9005.

(19) Fan, L.; Ziegler, T. *J. Phys. Chem.* **1991**, *94*, 6057; **1992**, *96*, 6937.

(20) Versluis, L.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 322.

(21) Fan, L.; Ziegler, T. *J. Chem. Phys.* **1991**, *95*, 7401.

(22) Wang, S.G.; Pan, D. K.; Schwarz, W. H. E. *J. Chem. Phys.* **1995**, *102*, 9296.

(23) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486.

(24) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

(25) Baerends, E. J.; Rozendaal, A. In *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry*; Veillard, A., Ed.; NATO ASI series C176; Reidel: Dordrecht, 1986, p 159.

(26) Ziegler, T. In *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry*; Veillard, A., Ed.; NATO ASI series C176; Reidel: Dordrecht, 1986; p 189.

(27) Chung, S.-C.; Kruger, S.; Pacchioni, G.; Rosch, N. *J. Chem. Phys.* **1995**, *102*, 3695.