

The formation, photodissociation, and bond structure of cobalt–sulfur cluster ions

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The formation and photodissociation of cobalt–sulfur cluster ions (Co_nS_m^+) produced by laser ablation on a tablet of well-mixed cobalt and sulfur powder were studied with a home-built tandem time-of-flight (TOF) mass spectrometer. In the mass spectrum, there are many intense peaks of more stable cluster ions Co_nS_m^+ signified as follows: $n=2-5, 7, m=n-1$; $n=6, 8-11, m=n-2$; $n=12-13, m=n-3$; $n=14-16, m=n-4$. The photolysis of the mass-selected cluster ions was performed with a 248 nm excimer laser. The dissociation patterns support the above composition results. Previous theories about clusters do not explain the experimental results. A relationship between the electron number and orbital number of more stable clusters was recognized. *Ab initio* calculations were performed on two small cluster ions to determine stable geometries. © 1994 American Institute of Physics.

INTRODUCTION

The distribution of stable clusters might change appreciably depending on the conditions of the cluster's production. On laser ablation of a solid sample, the local temperatures produced by the laser are high enough to evaporate any element, and clusters can be formed after collisions of atoms in the gas phase when cooled by supersonic expansion. By this method, a variety of clusters including homoclusters and heteroclusters of metal and nonmetal elements have been produced. Binary clusters of transition metals and sulfur have attracted much more attention because of their important applications in the field of superconductivity, biological processes, catalytic processes, etc.¹

Transition metal and sulfur binary clusters, such as Ta_nS_m^+ ,² Fe_nS_m^+ ,³ and $(\text{MnS})_m^+$,⁴ have been studied in our laboratory. Some salient characteristics about the stability and photolysis of those clusters were reported. We have found that, with different transition metals, the stable binary cluster ions have different compositions and give different photolytic products. The reason might be closely related to the number of valence electrons of the metal. In this paper, we report the results of Co_nS_m^+ clusters.

EXPERIMENT

The samples were prepared with cobalt (purity 99%) and sulfur (purity 99%) powders, mixed in different atomic ratios and pressed to form tablets.

Experiments were performed on a homemade tandem time-of-flight mass spectrometer (TOF-MS), described in detail elsewhere.⁵ In brief, the second harmonic of a Nd:YAG laser (532 nm, 5–10 mJ/pulse, 10 pulse/s) was focused on the surface of a tablet held in the vacuum chamber at 10^{-6} Torr to produce the cluster ions. The cluster ions were extracted and accelerated by a pulsed voltage of 1.2 kV and then drifted in a field-free region 3.5 m long. The ions were

detected by a dual microchannel plate detector and recorded to give the mass spectrum (first MS).

At the end of the field-free region, there was a mass gate which could be operated by a pulsed voltage for mass selection. A UV excimer laser (248 nm, 10 mJ/cm²) was used for the photolysis of the selected ions. The product ions and the remaining parent ions were accelerated perpendicular to the first stage MS with a voltage of 4.2 kV and drifted in a field-free region of 1.5 m. The ions were detected with another dual microchannel plate detector (second MS), and the signals were recorded with a transient recorder (10 MHz bandwidth). Typically, 1000–10 000 laser shots were accumulated and stored in an IBM-PC computer.

RESULTS AND DISCUSSION

Formation of cobalt–sulfur cluster ions

In our experiments, C^+ , O^+ , and H_2O^+ peaks have not been observed in the spectra. Thus, the effect of carbon and oxygen impurities could be ignored in the process of Co–S cluster formation. All cluster ions in the mass spectra consist of cobalt and sulfur only and can be symbolized as Co_nS_m^+ .

The experimental results show that the composition of the sample, i.e., the atomic ratio of Co and S, appreciably influences the distribution of the mass peaks in the mass spectrum. As a result, we divide the mass spectra of different atomic ratios of Co and S into two groups. The mass spectra of Co:S=1:1.8, 1:0.9, and 1:0.11 can be put in one group because the distribution of the cluster sizes (n, m) and the relative intensities of mass peaks in the mass spectra are similar. The spectrum of Co:S=1:1.8 is shown in Fig. 1(a). The mass spectra of Co:S=1:3.7 and 1:7.4 can be included in another group. The spectrum of Co:S=1:3.7 is shown in Fig. 1(b). In the spectra of this group, the number of S atoms, m , of the strong peaks can be much greater than the number of Co atoms, n . It can be inferred that there exist two types of sulfur atoms in Co–S clusters, those tightly bonded and those loosely bonded to the Co_nS_m^+ clusters.

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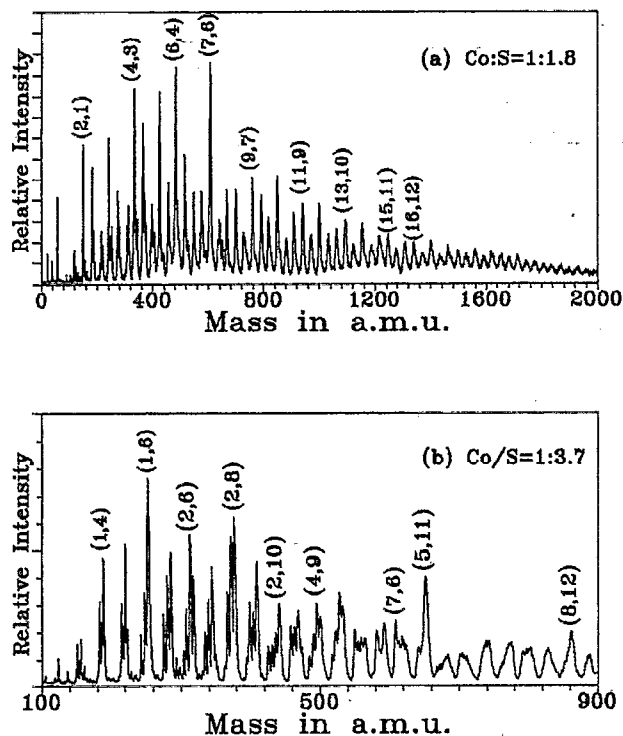


FIG. 1. The first stage TOF mass spectrum of Co-S cluster ions. (a) The molar ratio of the ablated sample is Co:S=1:1.8; (b) the molar ratio of the ablated sample is Co:S=1:3.7.

We first chose the mass spectrum of the sample with the atomic ratio Co:S=1:1.8 to study the relative stability of Co-S cluster ions. For the Co_5S_m^+ cluster group, as shown in Table I, the mass peak of Co_5S_4^+ was the highest while Co_5S_5^+ was the second highest. For samples of Co:S=1:0.9 and 1:0.11, Co_5S_4^+ is also the highest peak. It can be concluded that Co_5S_4^+ is the most stable product in the cluster series corresponding to $n=5$. Applying the same analysis to other cluster series ($n=2,3,4,6,\dots$), we can find the most stable cluster ion for each n value. In each case, the composition of the most stable cluster ion is similar for the above three Co:S compositions. As a result, only the mass spectrum of the sample with the molar Co:S=1:1.8 will be discussed.

In the mass spectrum of the sample Co:S=1:1.8, the largest cluster ions observed have masses about 2000 amu, although we could assign the cluster ions one by one, only

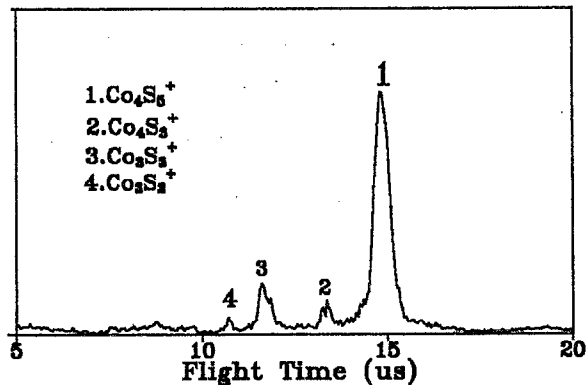


FIG. 2. The second stage TOF mass spectrum of Co_4S_5^+ photodissociation.

up to $\text{Co}_{16}\text{S}_{12}^+$ (1328 amu). The more stable cluster ions, i.e., the local more intensive peaks in the mass spectrum, have the following compositions:

$$n=2-5, 7, \quad m=n-1,$$

$$n=6, 8-11, \quad m=n-2,$$

$$n=12-13, \quad m=n-3,$$

$$n=14-16, \quad m=n-4.$$

The distribution of Co-S clusters is quite different from those of Mn-S⁴⁺ and Fe-S³⁺ clusters. The more stable clusters were assigned to be $n=m$ for Mn_nS_m^+ clusters and $n=m$ or $n=m+1$ for Fe_nS_m^+ clusters. The smoothly change of the difference ($n-m$) of the relative more stable Co_nS_m^+ clusters suggests that all Co-S cluster ions might follow a single bonding principle.

For samples of high sulfur composition Co:S=1:3.7 and 1:7.4, the m/n ratio for the mass peaks is considerably greater than for the low sulfur sample, one possible explanation is that the extra S atoms are attached to the Co atoms of the cluster core as ligands.

Photodissociation

Some species of Co_nS_m^+ cluster ions were selected individually by the mass gate in the tandem TOF mass spectrometer and irradiated by light from a 248 nm UV laser. A typical mass spectrum after photodissociation is shown in Fig. 2. The parent ion is Co_4S_5^+ and the product ions are Co_4S_3^+ ,

TABLE I. The relative intensities of Co_5S_m^+ cluster ions.

Atomic ratio of sample	Co_5S_3^+	Co_5S_4^+	Co_5S_5^+	Co_5S_6^+	Co_5S_7^+	Co_5S_8^+	Co_5S_9^+	$\text{Co}_5\text{S}_{10}^+$	$\text{Co}_5\text{S}_{11}^+$
1:0.11	0.16	1	0.10						
1:0.9	0.14	1	0.42						
1:1.8	0	1	0.43	0.19					
1:3.7	0	1	1.65	1.42	1.52	1.19	1.47	1.52	3.16
1:7.4	0	1	1.11	0.97	1.05	0.73	0.92	0.90	1.17

TABLE II. Photodissociation of Co-S cluster ions.

Parent ion	Photodissociation channel	Channel ratio ^a (%)	Parent ion	Photodissociation channel	Channel ratio (%)
CoS ₄ ⁺	→ CoS ₂ ⁺ + (S ₂) ^b	s ^c	Co ₆ S ₅ ⁺	→ [Co ₅ S ₄ ⁺ + (CoS)	9.8
CoS ₆ ⁺	→ CoS ₂ ⁺ + (S ₄)	4.2		[Co ₄ S ₃ ⁺ + (Co ₂ S ₂)	13.1
Co ₂ S ₅ ⁺	→ Co ₂ S ⁺ + (S ₄)	8.5	Co ₇ S ₆ ⁺	→ [Co ₅ S ₄ ⁺ + (CoS ₂)	2.8
Co ₂ S ₆ ⁺	→ Co ₂ S ₂ ⁺ + (S ₄)	2.9		[Co ₆ S ₄ ⁺ + (CoS ₂)	7.7
				[Co ₅ S ₄ ⁺ (Co ₂ S ₂)	4.9
Co ₃ S ₃ ⁺	→ [Co ₂ S ₂ ⁺ + (CoS)	7.1	Co ₇ S ₇ ⁺	→ [Co ₇ S ₅ ⁺ + (S ₂)	11.4
	[Co ₂ S ⁺ + (CoS ₂)	12.6		[Co ₆ S ₄ ⁺ + (CoS ₃)	8.7
Co ₃ S ₄ ⁺	→ Co ₃ S ₂ ⁺ + (S ₂)	21.0		[Co ₅ S ₄ ⁺ S ₄ ⁺ + (Co ₂ S ₃)	6.0
Co ₃ S ₅ ⁺	→ [Co ₂ S ₃ ⁺ + (CoS ₂)	6.4	Co ₈ S ₆ ⁺	→ [Co ₇ S ₆ ⁺ + Co	15.5
	[Co ₂ S ⁺ + (CoS ₄)	3.2		[Co ₆ S ₄ ⁺ + (Co ₂ S ₂)	7.7
Co ₄ S ₃ ⁺	→ [Co ₂ S ₂ ⁺ + (Co ₂ S)	16.1		[Co ₅ S ₄ ⁺ + (Co ₃ S ₂)	3.6
	[Co ₂ S ⁺ + (Co ₂ S ₂)	12.4		[Co ₄ S ₄ ⁺ + (Co ₄ S ₂)	2.1
Co ₄ S ₅ ⁺	→ Co ₄ S ₃ ⁺ + (S ₂)	9.1		[Co ₄ S ₃ ⁺ + (Co ₄ S ₃)	3.6
	[Co ₃ S ₃ ⁺ + (CoS ₂)	15.2	Co ₈ S ₇ ⁺	→ [Co ₇ S ₇ ⁺ + Co	12.4
	[Co ₃ S ₂ ⁺ + (CoS ₃)	4.0		[Co ₇ S ₅ ⁺ + (CoS ₂)	8.7
Co ₅ S ₄ ⁺	→ [Co ₄ S ₄ ⁺ + Co	5.7		[Co ₆ S ₅ ⁺ + (Co ₂ S ₂)	4.3
	[Co ₄ S ₃ ⁺ + (CoS)	9.1		[Co ₆ S ₄ ⁺ + (Co ₂ S ₃)	4.3
	[Co ₃ S ₃ ⁺ + (Co ₂ S)	5.7			
	[Co ₂ S ₂ ⁺ + (Co ₃ S ₂)	5.7			
	[Co ₂ S ⁺ + (Co ₃ S ₃)	2.6			
Co ₅ S ₅ ⁺	→ Co ₅ S ₃ ⁺ + (S ₂)	5.5	Co ₉ S ₆ ⁺	→ [Co ₈ S ₆ ⁺ + Co	14.4
	[Co ₄ S ₃ ⁺ + (CoS ₂)	4.1		[Co ₇ S ₆ ⁺ + (Co ₂)	11.6
	[Co ₄ S ₂ ⁺ + (CoS ₃)	s		[Co ₆ S ₄ ⁺ + (Co ₃ S ₂)	5.8
	[Co ₃ S ₂ ⁺ + (Co ₂ S ₄)	s	Co ₉ S ₇ ⁺	→ [Co ₇ S ₆ ⁺ + (Co ₂ S)	12.7
	[Co ₂ S ₂ ⁺ + (Co ₃ S ₃)	s		[Co ₇ S ₅ ⁺ + (Co ₂ S ₂)	7.9
				[Co ₆ S ₄ ⁺ + (Co ₃ S ₃)	4.2
				[Co ₅ S ₄ ⁺ + (Co ₄ S ₃)	4.2
Co ₆ S ₄ ⁺	→ Co ₅ S ₄ ⁺ + Co	s	Co ₉ S ₁₁ ⁺	→ Co ₉ S ₉ ⁺ + (S ₂)	13.4

^aChannel ratio = $I_a / (\sum I_a + I_p)$. I_a : The intensity of the product ion. I_p : The intensity of the parent ion.

^bThe bracket indicates that the neutral part might be S₄, two S₂, or four S atoms, the real state of which cannot be determined in the experiment.

^cThe peak is too small to be measured.

Co₃S₃⁺, and Co₃S₂⁺. We have summarized the results of photodissociation of different cluster ions in Table II.

In general, when cluster ions contain many more sulfur atoms than cobalt atoms, such as CoS₄⁺ or Co₂S₅⁺, the main

photodissociation channels are those corresponding to loss of S₂ or S₄ until the numbers of Co and S atoms remaining in the daughter ion are similar. This result might be taken as a evidence that the kicked-out sulfur atoms in the clusters are

loosely attached. When the numbers of Co atoms and S atoms are similar in the parent cluster ion, the photolysis paths can be a loss of Co, S₂, CoS, Co₂S, CoS₂, etc. Another observation is that the product ions of photodissociation generally appear to be the more stable ions in the first stage TOF-MS. For example, the photodissociation product of Co₉S₆⁺ can be Co₈S₆⁺, Co₇S₆⁺, Co₆S₄⁺, or Co₅S₄⁺. In other words, photodissociation produces cluster ions found to be stable in the initial cluster distribution.

The structure and bonding of cobalt-sulfur cluster ions

To understand the structure of clusters is a difficult problem. It is impossible to ascertain the structure by the information from the first stage mass spectra and the photolysis only. The structure of Co_nS_m clusters cannot be similar to the crystal structures of cobalt-sulfur compounds⁶ CoS, CoS₂, Co₃S₄, etc., because the compositions of the more stable Co-S clusters reported here are $m < n$, i.e., the number of S atoms is smaller than the number of Co atoms.

We tried to explain the bonding in the Co-S clusters according to earlier theories. There are two types of theories for the bonding of clusters of transition metals with accompanying ligands. The first one is the well-known electron counting rule (polyhedral skeletal electron pair theory, PSEPT),⁷ which works quite well for the clusters of transition metals with ligands like carbonyl, etc. The second one, proposed by Cotton,⁸ is for transition metal-noncarbonyl clusters, such as the type of [M₆X₈], [M₆X₆] clusters (M—transition metal, X—ligand). According to Cotton, only the *d* orbitals of the transition metal are considered to form the molecular orbitals of the clusters, and one *d* orbital is for linking a ligand and the other four *d* orbitals are for M-M bonding. We have tried to apply both theories to Co-S clusters without success. For example, if we use Cotton's theory for the cluster ion Co₆S₄⁺, the cluster has at least 30 electrons for M-M bonding, but the bonding orbitals permitted by symmetry are 12 at most, in which only 24 electrons can be contained. The above analysis shows that the Co-S clusters exist in a new kind of bonding state and structural configurations.

Freas *et al.* reported the study of Co-O clusters.⁹ Most Co-O cluster ions have the composition of [Co(CoO)_n]⁺ or [CoO]_n⁺. In order to explain these results, the bonds in Co-O clusters were assumed to be ionic, and the balance of electric charges played an important role in the change of composition when the number of CoO units is increased. The difference between Co-O and Co-S clusters is obvious, the CoS unit is not increased uniquely in the composition of Co-S clusters and sulfur is less electron-negative than oxygen. Therefore, the bonds in Co-S clusters are less ionic and more covalent.

If a modified electron counting method is applied to the more stable Co-S clusters, an interesting regulation about electron structure can be deduced. According to Wade's rules, each sulfur atom can donate four electrons to form the skeleton if a sulfur atom adopts a so-called the "μ₃-bridge" to bond with cobalt atoms.¹⁰ Then, the number (*N*) of total

TABLE III. The number of orbitals and number of electrons of Co-S cluster ions.

More stable cluster ions	Total number of <i>s</i> and <i>d</i> orbitals of Co atoms	Total number of skeletal electron (<i>N</i> -1)
Co ₂ S ⁺	12	21
Co ₃ S ₂ ⁺	18	34
Co ₄ S ₃ ⁺	24	47
Co ₅ S ₄ ⁺	30	60
Co ₆ S ₄ ⁺	36	69
Co ₇ S ₆ ⁺	42	86
Co ₈ S ₆ ⁺	48	95
Co ₉ S ₇ ⁺	54	108
Co ₁₀ S ₈ ⁺	60	121
Co ₁₁ S ₉ ⁺	66	134
Co ₁₂ S ₉ ⁺	72	143
Co ₁₃ S ₁₀	78	156
Co ₁₄ S ₁₀ ⁺	84	165
Co ₁₅ S ₁₁ ⁺	90	178
Co ₁₆ S ₁₂ ⁺	96	191

skeletal electrons of cluster Co_nS_m can be calculated according to the equation

$$N = n \times (7 + 2) + m \times 4.$$

7 and 2 refer to the 3*d* and 4*s* electrons of a cobalt atom and 4 for 3*p* electrons of a sulfur atom.

The calculation results of skeletal electrons and the total number of 3*d* and 4*s* orbitals of cobalt atoms in the relative stable cluster ions are listed in Table III. From the table, it can be found that the total skeletal electrons are approximately twice the sum of 3*d* and 4*s* orbitals in Co atoms. The deviations are within two electrons except Co₂S⁺, Co₆S₄⁺, and Co₁₄S₁₀⁺. This relation implies that there may exist an unified bonding rule for the naked Co-S cluster which is certainly different from former PSEPT. The relation could be named the "12-electron regulation" instead of the 18-electron rule. Comparing with carbonyl coordination compounds, the sole difference is the end group. In an organometallic compound, the metal *s* and *p* orbitals are commonly considered to be tied up in bonding to the ligands.¹¹ It is possible that the metal 4*p* orbitals remain inert in clusters due to a lack of ligands. The *d* and *s* orbitals of transition metals form the bonds, which is the reason for the "12-electron regulation."

Ab initio calculation

Two smaller cluster ions, Co₂S⁺ and Co₃S₂⁺, were selected for quantum-mechanical calculation. STO-3G¹² was chosen as the basis, with RHF¹³ and UHF¹⁴ self-consistent field methods for different electronic configurations. The Berny method¹⁵ was used for optimization of structural configuration. In order to test the precision of the STO-3G basis in describing the clusters, we first optimized the Co-O bond length and compared it with the published value as the value of the Co-S bond length that has not been published.

The optimized bond length of Co-O: 1.581 Å; the ground state: ⁴Δ₁.

The experimental value published:¹⁶ 1.631 Å; the ground state: ⁴Δ₁.

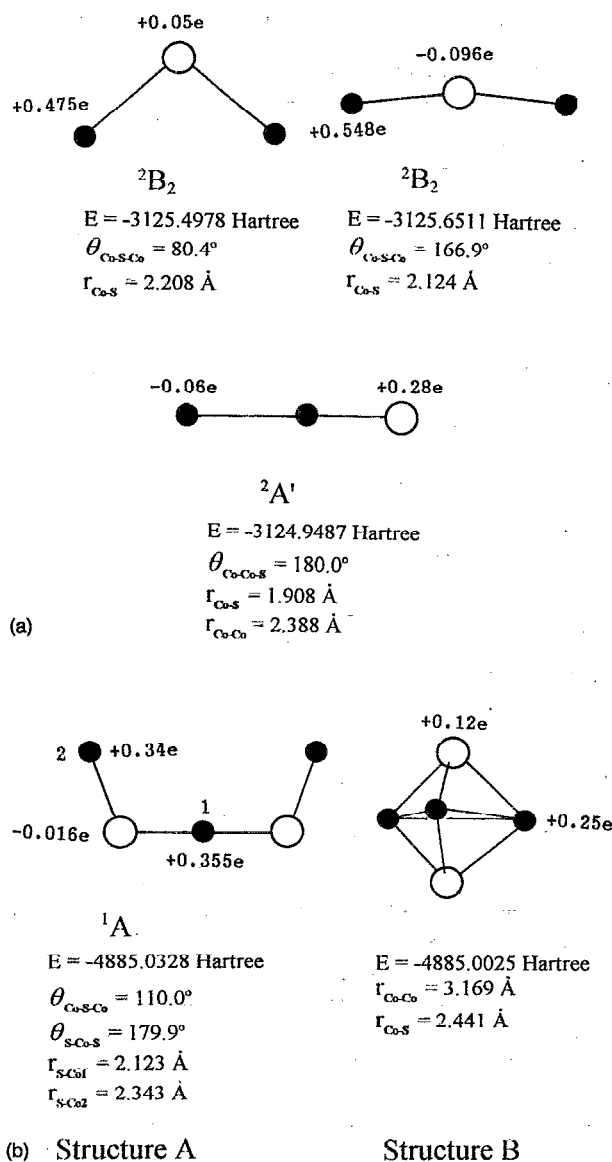


FIG. 3. The optimized configurations of two cluster ions by *ab initio* calculation. Filled circles are for cobalt atoms, circles for sulfur atoms. (a) Co_2S^+ ; (b) Co_3S_2^+ .

The above result indicates that the STO-3G basis can be used for calculation.

For Co_2S^+ , three structural models are assumed, and the results of calculation are shown in Fig. 3(a). Two of the configurations have C_{2v} symmetry with the sulfur atom acting as a bridge between the two cobalt atoms. The configuration without Co–Co interaction is more stable than the one with Co–Co interaction. The third configuration is of $C_{\infty v}$ symmetry, with two cobalt atoms interacting directly without sulfur bridge, and the structure becomes linear after optimization. Its stability is less than the other two. From the above results, it is suggested that the bonding between Co and S is the main source of Co_2S^+ stability. In the most stable configuration, the calculated bond length between Co and S is 2.134 Å, similar to that in the organometallic compounds

(2.10–2.30 Å).¹⁷ From the calculation, the Co–S bond in Co_2S^+ is more covalent than Co–O.¹⁸

The optimized configuration of Co_3S_2^+ was also calculated for two models: an open circle (A) and a closely packed structure (B). The results of calculation are shown in Fig. 3(b). In configuration A, two sulfur atoms act as bridges between the Co atoms, and the optimization makes the three Co atoms separate and the interaction between them is very weak. The configuration B is similar to the core in organometallic compounds and has D_{3h} symmetry. Unfortunately, the electronic state of structure B was not obtained from the calculation because of the complexity of the orbital symmetry. These two structures have similar stability. The average Co–S bond length in structure A is 2.23 Å, which is consistent with the normal value in organometallic compounds.¹⁷ The Milliken analysis supports the conclusion that the bond between Co and S is more covalent and the interaction of Co–Co is quite weak. From the calculation, it could be supposed that the interaction of Co–Co will be decreased further for the clusters with more sulfur atoms, and the Co–S and S–S bonding might be important in this sort of cluster.

For larger clusters, the structural model of Co_8S_6 was reported from the study of pentlandites.¹⁹ Burdett *et al.*²⁰ and Hoffman *et al.*²¹ calculated the electronic structure using EHMO (extended Hückel molecular orbital) and X_α methods, respectively. In this structure, the metal atoms occupy cubic corners within the sulfur matrix and the cluster has the symmetry I_h . Calculations^{20,21} showed that the d – d orbital interaction between metal atoms is important in the bonding of the clusters. Although the structural model may be correct, the outer environment will induce the change of bond length, which is always crucial for the characteristic of bonding. Even so, a simple structural model of Co–S clusters can be proposed: there are no sulfur atoms as end ligands in the relative stable clusters, the sulfur atoms as bridges link the cobalt atoms together, and the cobalt atoms do not have direct interaction.

In Fig. 1(b), there are much more S atoms in high peak cluster ions. We propose that the extra S atoms form end ligands of Co atoms in the clusters to fulfill the higher energy p orbitals of Co atoms. The sulfur ligand will be lost first on laser photolysis. The S atoms acting as an end ligand may make the total skeletal electron number of the cluster follow the 18-electron rule.

CONCLUSIONS

The Co–S cluster ions formed by laser ablation were studied and some of them were photolyzed by a UV laser. In the study of stability of binary clusters and heteroclusters as reflected in the intensity of peaks in the mass spectrum, the sample composition must be considered. The experimental results show that the composition of the most stable Co–S cluster ions form a regular pattern. An empirical regulation for the relation between electron number and orbital number of the more stable Co–S clusters was proposed.

ACKNOWLEDGMENT

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