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Electron distribution and intracluster reaction in $[\text{Na}_n(\text{CS}_2)_2]^-$ negative ion clusters

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Abstract. We have studied excess electron distributions of binary cluster negative ions consisting of sodium atoms and carbon disulfide molecules, $\text{Na}_n(\text{CS}_2)_2^-$ ($n = 1$ and 2) by using photoelectron spectroscopy and quantum chemical calculations based on the density functional theory (DFT). The photoelectron spectra indicate the existence of at least two isomers for both $n = 1$ and 2 anions. From the DFT calculations, mainly two types of isomers are found to coexist in the $\text{Na}(\text{CS}_2)_2^-$; one has a van der Waals (vdW) type CS_2 dimer core and another has a covalently bonded C_2S_4 core, both of which were known for CS_2 molecular cluster anions. In the latter isomers, the C_2S_4 portion possesses almost two electrons, which is caused by the valence electron transfer from the Na atom. Also for $n = 2$, we found the isomers of vdW and covalently bonded types. In the isomers with covalently bonded core, the C_2S_4 portion has more than two electrons, an excess electron and double valence-electron transfer from both of the sodium atoms.

PACS. 36.40.-c Atomic and molecular clusters – 36.40.Mr Spectroscopy and geometrical structure of clusters – 82.33.Fg Reactions in clusters

1 Introduction

Binary systems consisting of metal atoms and molecules are especially important in relation to the electron transport phenomena in nano-meter-sized materials. Spatial distribution of an excess and/or valence electron and electronic state-energy levels in these materials serve key roles to the appearance of useful properties in electronics. Gas-phase clusters of such binary systems are anticipated to be simplified models for the nano-materials and nano-sized junctions, where more basic information on electronic properties is necessary. However, a limited number of binary systems have been investigated in the gas-phase clusters [1]. As an example of the model cluster systems, Na- CS_2 binary clusters have been investigated in this study, following our recent study on $\text{Na}_n(\text{CS}_2)$ cluster anions [2]. The two constituent species are known to have close electron affinities; 0.55 eV for Na [3] and ~ 0.6 eV for CS_2 [4]. The spatial distribution of the excess electron in this system is important because it has a close relationship with the electron mobility from the metal anode to the nano-device in actual usage.

In the gas-phase CS_2 cluster anions, more than two geometrical isomers were suggested experimentally [5–7] and theoretically [8]; van der Waals (vdW) type $\text{CS}_2\text{-CS}_2^-$ and covalently bonded C_2S_4^- are the representative core structures of the isomers. The covalent dimer anion was

suggested to be generated by the electron attachment to the molecular clusters. Tetrathiooxalate dianion ($\text{C}_2\text{S}_4^{2-}$) is also known to be obtained by chemical or electrochemical dimerization of CS_2 in the condensed phase [9–11], although this anion is unstable in the aerobic condition. This anion is also known as a ligand of transition metal complexes, and can be synthesized by the metal mediated reductive dimerization of CS_2 [12,13]. These complexes are stable enough in the air, and have attracted much attention as one- and two-dimensional nanostructured materials with metallic or semiconducting properties [14].

In the present study, we have investigated photoelectron spectroscopy of $\text{Na}_n(\text{CS}_2)_2^-$ ($n = 1$ and 2) negative ions. Observed band positions are compared with the transition energies for the optimized structures obtained in the quantum chemical calculations based on density functional theory (DFT). Charge distributions in the negative ions and neutral states of the calculated isomer structures are discussed by categorizing into several types. The stabilities and electron acceptabilities of the isomers, which are dependent on the ion core, are also discussed.

2 Experimental set-up and calculations

Details of the experimental set-up were described in the previous papers [2,15,16]. The apparatus consists of three-stage differentially evacuated chambers, which include a cluster anion source, a time-of-flight (TOF) mass

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spectrometer with pulsed acceleration electrodes, and a magnetic-bottle photoelectron spectrometer. Na-CS₂ negative ion clusters were produced by a laser vaporization source. The produced anions were accelerated to ~ 700 eV by two-stage pulsed electric fields, and passed through a field-free region of 1.6-m length. Mass separated ions were detected by a dual microchannel plate (MCP; Hamamatsu, F4655) at the end of the flight tube. For obtaining photoelectron spectra (PES), ions with a given mass-to-charge ratio were selected by a mass gate composed of deflection plates. Selected ions were subsequently decelerated by pulsed potential switching method before entering the detachment region, in order to avoid Doppler broadening in the photoelectron spectra. Decelerated anions were irradiated with a third harmonic of another Nd:YAG laser (Spectr Physics, GCR150) at the center of the photoelectron spectrometer. Detached electrons were collected by a magnetic-bottle effect, where heterogeneous magnetic field was created from a permanent magnet (ca. 800 G at the detachment region) and a solenoid (10 G). After traveling a weak magnetic field region of 1.2-m length, these electrons were detected by another MCP (Hamamatsu, F1552-21S). Electron energy was calibrated against the reported electron affinity of Na (0.548 eV) [3]. Resolution of the present photoelectron spectrometer was estimated to be 50 meV for the 2.65-eV peak of the Na⁻ ion [2].

Sample disk of sodium (Rare Metallic Co., 99.9% pure) was made under nitrogen atmosphere in a vacuum dry box in order to avoid reactions with water in the air. Carbon disulfide (Nacalai, 99% pure) was used without further purification.

Quantum chemical calculations based on DFT were also performed in order to obtain the geometrical structures and electron distribution of the Na_{*n*}(CS₂)₂⁻ (*n* = 1 and 2) cluster anions and neutrals by using DFT program of the GAUSSIAN98 package. Vertical detachment energies (VDEs) and electron affinities (EAs) of the clusters were estimated from the energy differences between negative ions and the corresponding neutrals. The basis set of 6-311+G(d) and the correlation/exchange potential of B3LYP was utilized in the present calculation. Geometrical optimization of the present binary clusters was started from optimized (CS₂)₂⁻ structures reported by Sanov, Lineberger, and Jordan [8]. As for Na₂(CS₂)₂⁻, we performed geometrical optimization only for the negative ions to obtain VDEs. Natural population analysis was also made for the optimized structures.

3 Results and discussion

3.1 Photoelectron spectra (PES)

PES of (CS₂)₂⁻ and Na_{*n*}(CS₂)₂⁻ are shown in Figure 1 along with those of (CS₂)⁻ and Na_{*n*}(CS₂)⁻ which were recently reported by the authors [2]. The present spectrum of (CS₂)₂⁻ has two bands peaking at 1.64 and 2.64 eV, which is consistent with that reported by Nagata and coworkers [5]. However, relative intensity of the two bands,

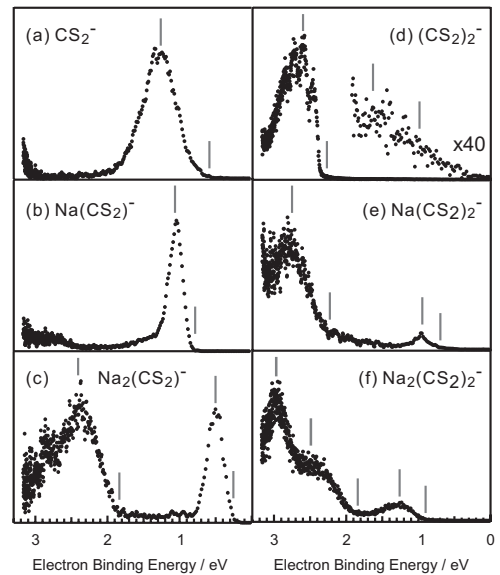


Fig. 1. Photoelectron spectra of Na_{*n*}(CS₂)_{*m*}⁻ (*n* = 0–2, *m* = 1, 2).

Table 1. Observed electron affinities (EAs) and vertical detachment energies (VDEs) of Na_{*n*}(CS₂)₂⁻.

	Assignment	EA / eV	VDE / eV
<i>n</i> = 1	1-A	0.71	0.95
	1-B	2.35	2.80
<i>n</i> = 2	2-A	0.90	1.26
	2-B	1.84	2.49
	2-C	~ 2.5	2.97

which are known to arise from two different isomer structures, was quite different from the previous study; intensities of the bands were comparable in reference [5], although the intensity of the 1.7-eV band was about two orders of magnitude smaller than that of the 2.7-eV band in the present spectrum. This discrepancy is probably due to the difference of the cluster source; cold clusters were formed in reference [5] by the electron attachment in the expansion region of the molecular beam, whereas the present laser-vaporization source may produce cluster anions with higher internal energy. Thus the photodetachment signal peaking at 2.64 eV from the most stable isomer is predominant in the present spectrum. This discussion is consistent with the results of stagnation-pressure dependence in reference [5].

Several bands were separately observed in the PES of Na_{*n*}(CS₂)₂⁻ as shown in Figures 1e and 1f and summarized in Table 1. For *n* = 1, two separated bands were observed with peak positions of 0.95 eV (band 1-A) and 2.80 eV (band 1-B). The intensity of the band 1-B is higher than that of 1-A in the figure, although the relative intensity was found to vary with the cluster source conditions. However the detailed propensity of such dependence could not be obtained because of the contribution of various parameters to the source conditions. Anyway, these two bands were tentatively assigned to those from at least

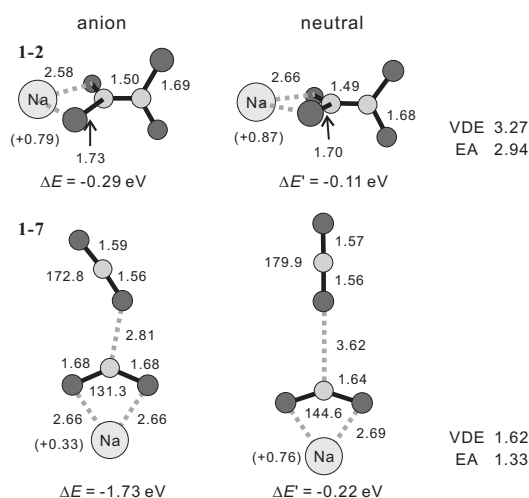


Fig. 2. Representative optimized structures of cluster anions and corresponding neutrals for $\text{Na}(\text{C}_2\text{S}_4)$ and $\text{Na}(\text{CS}_2)_2$. Bond lengths and angles are shown in Å and degrees, respectively. The energy difference (ΔE and $\Delta E'$) for each isomer from the most stable isomer of the anion or the neutral is also shown in eV. ΔE and $\Delta E'$ correspond to the energy difference of anion and neutral complexes, respectively. Values in parenthesis are natural charges on the sodium atom. Other structures are shown in the electronic-only material.

two different isomers. For $n = 2$ (Fig. 1f), two separated bands, 2-A and 2-C, were dominantly observed along with the additional peak located around 2.49 eV, band 2-B, as a shoulder of band 2-C. Relative intensity of these bands also varied with the cluster source conditions, so that these bands probably originate from several different isomers.

3.2 $\text{Na}(\text{CS}_2)_2^-$ ion

Several isomers of $(\text{CS}_2)_2^-$ were found in the theoretical study [8], which can be categorized with two types, vdW type like $(\text{CS}_2)-(\text{CS}_2)^-$ and covalently bonded C_2S_4^- anion. We confirmed the presence of these isomers at the present level of calculation. Optimized structures of $\text{Na}(\text{CS}_2)_2^-$ and their neutrals are shown in Figure 2 and in the electronic-only material, along with calculated VDEs and EAs. We found a neutral isomer structure corresponding to each anion, except for the **1-5** and **1-6** isomers in the figure; these two anions have a common neutral structure. All isomers are also categorized with two types by the structure of $(\text{CS}_2)_2$ portion, covalently bonded C_2S_4 (**1-1** to **1-4**) and vdW $(\text{CS}_2)-(\text{CS}_2)$ type isomers (**1-5** to **1-7**) in this figure. The former has higher VDE and EA values than the latter, although the isomer **1-4** has a smaller VDE than vdW type isomers **1-5** and **1-6**. From the comparison between experimental VDEs and EAs and calculated values, it is concluded that the band 1-A originates from the vdW type isomers and that the band 1-B is due to covalently bonded isomers. The isomer **1-7** is the most probable origin of the band 1-A from this comparison, although this isomer is the least stable. As for band 1-B,

the isomer **1-2** has the closest VDE value to the experimental one. However, the band 1-B has a broader feature than the width estimated from the calculation. Thus the possibility of the coexistence of the isomers of **1-1** to **1-3** cannot be ruled out.

Now we discuss the electron distribution of these possible isomers. In the isomers **1-1** to **1-3** with a covalently bonded C_2S_4 core, natural charges on the sodium atom were estimated to be nearly unity not only for the neutral species but also for the negative ion states. In the negative ions, the C_2S_4 core has a character of doubly charged anion, where an excess electron is localized on the C_2S_4 and the additional electron transfers from the sodium atom. Also from the electron distributions of the highest occupied molecular orbitals of these isomers, the electron is found to be mainly localized on the C_2S_4 portion. Therefore these isomers are concluded to have an ion-pair nature like $\text{Na}^+-\text{C}_2\text{S}_4^{2-}$. For the corresponding neutrals of isomer **1-1** to **1-3**, natural charges on the sodium atom are also almost unity. Thus the electron probably detaches mainly from the C_2S_4 portion.

All of the vdW type isomers, **1-5** to **1-7**, have local structures similar to the $\text{Na}(\text{CS}_2)^-$ complexes reported previously [2]. Furthermore the band 1-A has a peak energy, 0.95 eV, similar to that of $\text{Na}(\text{CS}_2)^-$, 1.05 eV. For the most probable candidate for the band 1-A, the isomer **1-7**, the negative ion complex has a slightly ionic nature like $\text{Na}^{\delta+}(\text{CS}_2)^{(1+\delta)-}-\text{CS}_2$, where the $\text{Na}(\text{CS}_2)$ portion resembles the $\text{Na}(\text{CS}_2)^-$ anion, as shown in Figure 2. The corresponding neutral isomer has further ionic nature like $\text{Na}^+(\text{CS}_2)^--\text{CS}_2$. Thus the electron probably detaches mainly from the $\text{Na}(\text{CS}_2)$ portion. More precisely, the electron is expected to detach from both of the Na and CS_2 portions in the $\text{Na}(\text{CS}_2)_2$ local structure of the $\text{Na}(\text{CS}_2)_2^-$ complex, as discussed in the detachment process for $\text{Na}(\text{CS}_2)^-$ [2].

3.3 $\text{Na}_2(\text{CS}_2)_2^-$ ion

We found twelve isomers of the $\text{Na}_2(\text{CS}_2)_2^-$ anion in the calculation as shown in Figure 3 and in the the electronic only material. These isomers can be categorized into four type structures, (I) $\text{Na}-\text{C}_2\text{S}_4-\text{Na}$ (**2-1–2-5**), (II) $\text{Na}_2-\text{C}_2\text{S}_4$ (**2-6–2-9**), (III) $\text{Na}_2-\text{CS}_2-\text{CS}_2$ (**2-10**), and (IV) others (**2-11, 12**).

Type I isomers are found to be more stable than other types and are the most probable candidate for the band 2-A, because they have VDE values around 1.5 eV except for isomer **2-4** (0.8 eV). All type I isomers have similar charge distribution; both of the Na atoms have large positive charges and the C_2S_4 core possesses two or three excess electrons.

Type II isomers are further categorized into two types, (a) both Na atoms directly interact with the C_2S_4 core (**2-6, 7**) and (b) one of the Na atom is directly bound to C_2S_4 (**2-8, 9**). The latter isomers have higher VDEs than the former, and the VDE value of the isomer **2-8** agrees well with the observed peak of band 2-C. Thus the isomer **2-8** is the most probable origin of the band. This

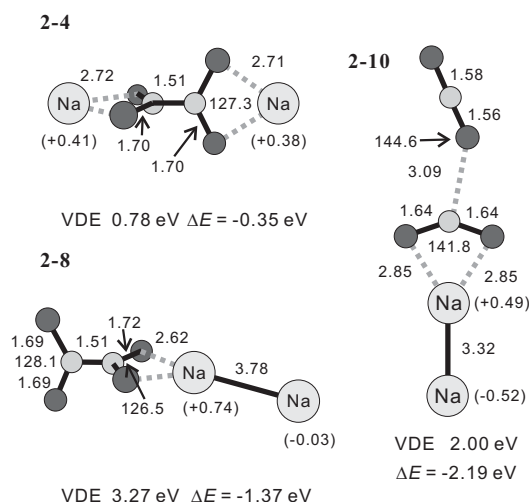


Fig. 3. Representative optimized structures of the $\text{Na}_2(\text{CS}_2)_2^-$ cluster anions. Bond lengths and angles are shown in Å and degrees, respectively. The energy difference (ΔE) for each isomer from the most stable isomer is also shown in eV. Values in parenthesis are natural charges on the sodium atoms. Other structures are shown in the electronic-only material.

isomer has a charge distribution having an ion-pair nature like $\text{Na}_2^+-\text{C}_2\text{S}_4^{2-}$, like the type I isomers. However one of the Na atom is weakly bound to the $\text{Na}(\text{C}_2\text{S}_4)$ complex, which shows marked contrast with the type I, and thus this isomer has a similar VDE with the isomer **1-2**.

The type III isomer **2-10** has a similar local structure with one of the isomers of $\text{Na}_2(\text{CS}_2)$ in reference [2], and thus it has a similar VDE with that complex. This isomer has a different ionic nature than the other $\text{Na}_2(\text{CS}_2)_2^-$ isomers; the Na_2 portion is almost neutral, and one of the CS_2 molecule has the excess electron. As for type IV isomers, **2-11** has a double ion-pair structure like $\text{Na}^+-\text{CS}_2^{2-}-\text{Na}^+-\text{CS}_2^-$, whereas **2-12** has a nature like $(\text{CS}_2)_2^--\text{Na}^+-\text{CS}_2^--\text{Na}$. The former has a similar core structure not only with the isomer **1-5** but also with the $\text{Na}(\text{CS}_2)^-$ complexes. The latter contains a structure similar to the isomer **1-6**. From the comparison of the VDEs and EAs, coexistence of these isomers cannot be ruled out although these are less stable than the isomers discussed above. At present we cannot clearly specify the isomers which were produced dominantly in the present cluster beam. However, several isomers with a characteristic properties, especially for the ionic nature as noted above, are suggested to coexist in the present study.

4 Conclusion

We have studied excess electron distribution in the binary cluster negative ions consisting of sodium atoms and carbon disulfide molecules, $\text{Na}_n(\text{CS}_2)_2$ ($n = 1$ and 2) by using photoelectron spectroscopy and DFT calculations. Some of the isomers obtained from the DFT calculations are found to reproduce the VDE and EA values obtained experimentally. In the $n = 1$ cluster, two types of iso-

mers are found to coexist: the cluster anions containing the covalently bonded C_2S_4 core have larger VDEs and EAs than the vdW type isomers having a weakly bonded $\text{CS}_2-\text{CS}_2^-$ portion. In the former isomers, C_2S_4 core possesses almost two excess electrons, which is caused by the additional electron transfer from the Na atom. Also in the latter isomers, the $(\text{CS}_2)_2$ portion is suggested to have roughly two electrons, where each CS_2 molecule accepts the excess electron and the valence electron of the Na atom. For the $n = 2$ anion, although we cannot clearly assign the observed PES, several characteristic isomers are found from the calculations. These isomers can be classified into four types. Among these, $\text{Na}_2(\text{C}_2\text{S}_4)^-$ type isomers, where the sodium dimer is bound to the C_2S_4 core, are found to have the largest VDEs, which are close to that of $\text{Na}(\text{C}_2\text{S}_4)^-$. On the other hand, the $[\text{Na}-(\text{C}_2\text{S}_4)-\text{Na}]^-$ type isomers have lowest VDEs, and the C_2S_4 ion core is suggested to have more than two electrons. The isomers containing CS_2 vdW dimers are found to have medium VDE values.

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