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Negative-ion photoelectron spectroscopy of Cu clusters reacted with NO molecules

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Abstract. Negative ions of copper clusters reacted with nitric oxide molecules are studied by mass-selected photoelectron spectroscopy. The series of the reacted cluster ions, Cu_nN^-, Cu_nNO^-, and $Cu_nNO_2^-$ are observed in the mass spectrum. Photoelectron spectra are obtained at 3.49 eV photon energy for Cu_nN^- ($n = 2$ and 3) and $Cu_nNO_2^-$ ($n = 1$ and 2). The photoelectron spectrum of Cu_2N^- contains a band structure analogous to that of Cu^- or Cu_2^-. From the expansion gas pressure dependence of the band peak intensity in the spectrum, it is concluded that Cu_2N^- has at least two isomers in the beam. One of the isomers is expected to have a structure in which the central ion is Cu^- or Cu_2^- and the residual atom(s) are weakly bound to the ion. For Cu_nNO^- ($n = 1 - 3$), we detected no electron signals with the detachment photon energy of 3.49 eV. The possible structure of $CuNO^-$ is discussed in the light of the present results and also on the basis of the recent results of the study of CuO_2^- by Wang and coworkers.

PACS. 36.40.-c Atomic and molecular clusters – 36.40.Cg Electronic and magnetic properties of clusters – 36.40.Mr Spectroscopy and geometrical structure of clusters – 36.40.Vz Optical properties of clusters – 36.40.Wa Charged clusters

1 Introduction

Electronic and geometrical structures of metal clusters have been one of the main subjects in cluster research for nearly two decades now [1–6]. Extensive studies have been devoted to this subject both experimentally [2–6] and theoretically [1, 3, 5, 6]. Especially for the clusters of atoms with one valence electron such as alkali metal and coinage atoms, the electronic shell model and the jellium model are found to give a reasonable explanation for the stability of the clusters [3, 5, 6]. The electronic structures of metal clusters are also discussed in relation to the reaction with some simple molecules: for example, the reactions of transition metal clusters with H_2 [7, 8] and Cu clusters with CO [9–15] are studied with reference to their electronic states. However, few studies were devoted until recently to the electronic structures of the systems consisting of metal clusters and a molecule, which is regarded as a model of the molecule adsorbed on a metal surface. In recent years, negative-ion photoelectron spectroscopy, which is a powerful technique for studying the electronic structures of size-selected neutral clusters, has been utilized for metal clusters reacted with simple adsorbates [16–21]. The extension of such studies is important so as to provide information about the number of the metal atoms contributing to adsorption, and thus to elucidate the adsorption mechanism on the bulk surface.

In the present study, copper clusters reacted with NO molecules are studied by negative-ion photoelectron spectroscopy. The adsorption of NO molecules on Cu surfaces has also been studied extensively [22], because of the practical interest in the development of catalysts that transform the NO_x species into nonpolutant products. It is known from electron spectroscopy and electron diffraction that the NO molecule adsorbed on a Cu surface dissociates at temperatures as low as 80 K [23–25]. The mechanism of this dissociative chemisorption has been partially discussed [15]; however, it is also important to investigate the electronic structure of the adsorbate experimentally for the model clusters of the NO adsorbed on a Cu surface, Cu_n-NO. As an initial step for the purpose, we have examined the photoelectron spectra of Cu_nN^- ($n = 1 - 3$), Cu_nNO^- ($n = 1$ and 2), and $Cu_nNO_2^-$ ($n = 1$ and 2). With the photon energy of 3.49 eV for electron detachment, we could detect no signal for the detachment of CuN^-, $CuNO^-$ and Cu_2NO^-. For Cu_2N^-, it is found from the dependence of the gas expansion pressure that at least two isomers are produced in our cluster source. The possible geometrical structure of one isomer of this ion is discussed in terms of a comparison with the photoelectron spectra of pure Cu_n^- clusters. Finally, from the results of photoelectron spectroscopy of Cu_nNO^- and $Cu_nNO_2^-$, the geometrical structure of these cluster ions is discussed.

2 Experiment

We have constructed a three-stage differentially evacuated chamber for the photoelectron spectroscopy of mass-selected cluster negative ions. Details of the experimental apparatus will be published elsewhere. We used a conventional setup for the laser vaporization metal cluster source, a time-of-flight type mass spectrometer for cluster size selection, and a magnetic-bottle type photoelectron energy analyzer [26,27]. Copper cluster anions were produced by a laser vaporization method: The output of the second harmonic of a Nd:YAG laser (Lumonics, HY400) was focused onto a rotating and translating copper rod inside a source block. The source block was attached to a pulsed valve (General Valve, Series 9, nozzle diameter 0.8 mm), from which He gas mixed with NO (1%) of 10 atm was expanded. The timings of the valve opening and the laser irradiation were set by a digital delay/pulse generator (Stanford Research, DG535) so that negative ions of the clusters were produced most efficiently. The ions produced were accelerated to 800 eV with a two-stage pulsed electric field in a Wiley–McLaren type time-of-flight (TOF) mass spectrometer. After flying 1.6 m in a field-free flight tube, the size distribution of the negative ions was monitored by dual microchannel plates (Hamamatsu, F-4655) set at the end of the ion flight tube. For the photoelectron spectroscopy, ions with a given mass-to-charge ratio were selected in the flight tube with a mass selector composed of deflection plates, to which a pulsed electric field was applied. The mass resolution of this mass selector is estimated to be ca. 30. Then the selected ions were decelerated before entering the detachment region, in order to prevent the Doppler broadening in the photoelectron spectra [27,28]. Finally the ions were irradiated with a third harmonic (355 nm, 3.49 eV) of another Nd:YAG laser (Lumonics, HY400) at the source of the magnetic-bottle photoelectron energy analyzer. Detached electrons were collected in the inhomogeneous magnetic field and detected by dual microchannel plates (Hamamatsu, F1552-23S) after the flight in a 2.5 m tube. The resulting photoelectron time-of-flight spectra were converted to energy spectra calibrated by Cu^- photoelectron spectra reported previously [29]. Though the magnetic-bottle type photoelectron spectrometer has the advantage that almost all the ejected electron can be collected in principle [26,27], the electron detection efficiency in our spectrometer was found to be rather low in the low electron energy region. This may be due to the high background pressure in the electron time-of-flight tube (typically 2×10^{-7} Torr) and/or the stray magnetic field. However we did not calibrate the intensity of the photoelectron signal here. Typical energy resolution was about 100 meV at the 1.23-eV peak in the photoelectron spectrum of Cu^-.

3 Results and discussion

3.1 Negative ion mass spectra

Figure 1 shows a typical TOF mass spectrum of negative ions produced by the laser vaporization source. In this spectrum negative ions of copper clusters associated with NO molecules and their fragment species are observed, in addition to the pure copper metal cluster anions, Cu_n^-: The main cluster series are attributed to Cu_nN^-, Cu_nNO^-, and $Cu_nNO_2^-$. Because the Cu atom has two isotopes with masses of 63 (69%) and 65 (31%), the Cu_nN^- and Cu_nNO^- ions may partly overlap with the Cu_nO^- and $Cu_nO_2^-$, respectively. However, we could detect no signal of CuO^- and CuO_2^- ions from the peak shapes around these mass-to-charge ratios in the mass spectrum. Therefore we expect that only the Cu_nN^- and Cu_nNO^- ions are efficiently produced in the present study. Also the intense signal of NO_2^- was observed in the mass spectrum. The NO_2 molecule can be easily produced from the thermal dissociation of NO in the "microplasma" region of the laser vaporization source. In addition, we cannot exclude the possibility that small amounts of NO_2 may be contained in the NO sample. In the production of the reacted Cu cluster ions observed in the mass spectrum, the reactant molecules coexist in the metal cluster source and may dissociate by nonresonant multiphoton absorption of the vaporization laser or by thermal reaction at the source in the present experiment, in contrast to the fast flow reactor usually used in chemical reaction studies of clusters [30]. Therefore it is difficult to discuss further the formation mechanism of the reacted Cu cluster ions.

3.2 Negative ion photoelectron spectra

3.2.1 Cu_nN^-

Photoelectron spectra of Cu_n^- and Cu_nN^- for $n = 1 - 3$ are shown in Fig. 2a–f. The spectra of Cu_n^- have same features as those reported previously [29,31–33], except for the small signal intensity in the low electron energy region, as mentioned in the previous section. The spectrum of Cu^- (Fig. 2a) consists of an intense band at 1.23 eV and two weak bands at 2.7 and 3.0 eV; these three bands correspond to the transitions from Cu^- $^1S(3d^{10}4s^2)$ to Cu $^2S(3d^{10}4s^1)$, Cu $^2D_{5/2}(3d^94s^2)$, and Cu $^2D_{3/2}(3d^94s^2)$, respectively. In the Cu_2^- spectrum (Fig. 2b) also exhibits three bands peaking at 0.9, 2.6 and 3.0 eV; the former two bands can be assigned to the transitions from Cu_2^- $^2\Sigma_u^+$ to Cu_2 $^1\Sigma_g^+$ and Cu_2 $^3\Sigma_u^+$ states, respectively. The last band can be assigned to the overlapped transitions to higher Cu_2 $^3\Pi_u$ and $^1\Sigma_u^+$ states [32]. The spectrum of Cu_3^- (Fig. 2c) has a band at 2.3 eV. The equilibrium structure of Cu_3^- is linear and thus this band can be assigned to the transition from the linear Cu_3^- $^1\Sigma_g^+$ to the linear Cu_3 $^2\Sigma_u^+$ state [31].

No detached electron signal from the CuN^- ion was observed under excitation with a photon energy of 3.49 eV as shown in Fig. 2d. Electron affinities of Cu and N atoms are reported to be 1.23 [29,34] and −0.07 eV [35], respectively. Therefore the excess electron may be localized in

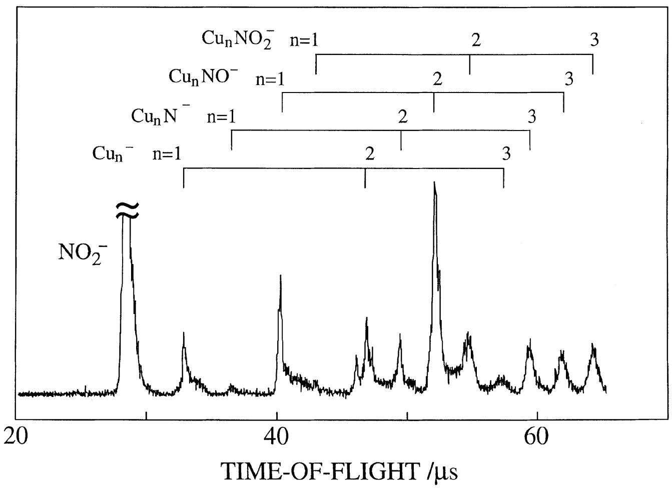

Fig. 1. Typical time-of-flight mass spectrum of negative ions directly produced in the laser vaporization of the Cu rod and by the expansion with 10 atm He mixed with NO(1%).

the vicinity of Cu atom in the CuN^- anion. However, the present result indicates that CuN^- has a vertical electron detachment energy more than 3.3 eV. This lower limit is estimated by taking account of the electron collection efficiency in the present spectrometer. There is also a possibility that no signal was detected due to the low density of the CuN^- ion and the low detection efficiency of our spectrometer. However, no data on this species is available in the literature so far.

In the case of Cu_2N^- (Fig. 2e), we obtained a photoelectron spectrum which consists of a peak at 1.1 eV and at least four peaks at 2.5–3 eV. This feature of the spectrum appears to resemble those of the spectra of Cu^- or Cu_2^-, except for the several peaks observed in the 2.5–3 eV region. In addition to these observations, the relative intensities of the peaks appearing in the Cu_2N^- spectrum are found to be sensitively dependent on the stagnation pressure in the cluster source. We controlled the effective gas expansion pressure from the pulsed valve by changing the pulsed voltage applied to the valve. The expansion gas pressure is easier to control than the stagnation pressure of the mixed sample gas, though it is difficult to discuss the source condition quantitatively. The results of the expansion pressure dependence of the photoelectron spectra are shown in Fig. 3. With increasing the gas pressure, the intensities of the peaks at 1.1, 2.7 and 3.0 eV (peaks indicated by circles in Fig. 3) are found to decrease relative to those of the other peaks in the 2.5–3 eV region (those indicated by asterisks). This result indicates that the Cu_2N^- anions consist of at least two different isomers, and that the branching fractions between the isomers are strongly dependent on the cluster temperature. One isomer, whose branching fraction decreases with increasing expansion gas pressure, has three bands peaking at 1.1, 2.7, and 3.0 eV (indicated by circles in Fig. 3). These band peak positions appear to correspond to those in the Cu^- or the Cu_2^- photoelectron spectrum. Thus it is concluded that the electronic structure of this isomer resembles that of Cu^- or Cu_2^-. From this consideration two possibilities are raised for the geometrical structure of this isomer: One is a structure in which CuN weakly ligates to the Cu^- ion, and the other involves a N atom that is weakly bound to Cu_2^-. We cannot determine which structure is more probable at present, however, this isomer is considered to be metastable from the dependence on the expansion pressure. In contrast, another isomer (characterized by the peaks indicated by asterisks in Fig. 3) is considered, from the expansion pressure dependence, to be more stable. In this isomer the Cu and the N atoms may be tightly bound to one another to form a stable structure.

The photoelectron spectrum of the Cu_3N^- ion (Fig. 2f) has the following features: One strong band is observed at 2.9 eV with weak shoulders at 1.7 and 2.1 eV. The band at 2.9 eV may correspond to the band observed in the spec-

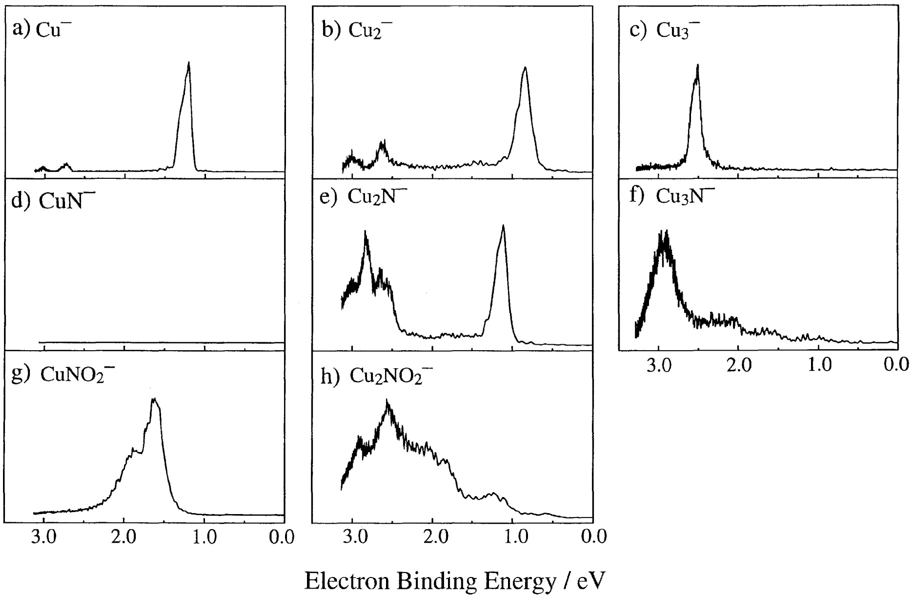

Fig. 2. Photoelectron spectra of Cu_n^- ($n = 1-3$), (a–c), Cu_nN^- ($n = 1-3$), (d–f), and $Cu_nNO_2^-$ ($n = 1$ and 2) (g, h). The photon energy of the detachment laser is 3.49 eV (third harmonic (355 nm) of the Nd:YAG laser).

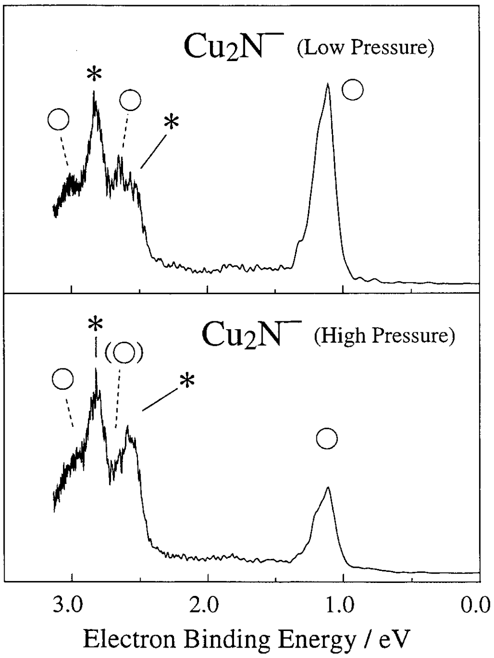

Fig. 3. Photoelectron spectra of Cu_2N^- obtained under (a) high, and (b) low expansion gas density. The peaks indicated by circles and those indicated by asterisks are attributable to the bands of two independent isomers (see text).

trum of Cu_3^-. However, an experiment with a higher detachment photon energy is necessary to elucidate the electronic and geometrical structure of this ion further.

3.2.2 Cu_nNO^- and $Cu_nNO_2^-$

No photoelectron signal was detected for the detachment of Cu_nNO^- for $n = 1 - 3$ with the photon energy of 3.49 eV. This result means that these cluster ions have vertical detachment energies larger than 3.3 eV, as in the case of CuN^-. The NO molecule has a low electron affinity of 0.024 eV [36], and thus such large vertical detachment energies of the cluster ions do not reflect the electronic structure of the NO molecule.

A possible geometrical structure of the $CuNO^-$ ion is suggested from the recent study on the photoelectron spectroscopy of CuO_2^- reported by Wang and coworkers [18]. In their study, the CuO_2^- complex has been found to have two isomers: One isomer has a structure in which the O_2 molecule is bound weakly to the Cu atom, $[Cu(O_2)]^-$, and the other is an anion of linear copper dioxide, $OCuO^-$. The electron affinities of the two isomers have been determined to be 1.5 eV for $Cu(O_2)$ and 3.46 eV for OCuO, respectively. The value of the electron affinity of the latter species in which O_2 is adsorbed dissociatively is much larger than that of the O_2 molecule, 0.44 eV [37], as in the present case of $CuNO^-$. Therefore, also for the $CuNO^-$ ion, the NO molecule may dissociate and become tightly bound to the Cu atom with a structure in which both N and O atoms attach to the Cu atom separately.

Photoelectron spectra of $Cu_nNO_2^-$ for $n = 1$ and 2 are shown in Fig. 2g and 2h, respectively. We also obtained a spectrum of the NO_2^- ion, which has only a broad band with threshold at 2.3 eV (not shown). This electron detachment threshold is in good agreement with those reported so far [38, 39], though the vibrational progression cannot be resolved in our spectra due to the lack of resolution of the electron energy analyzer. The spectra of $CuNO_2^-$ and $Cu_2NO_2^-$ consist of broad bands which correspond to neither the electronic structure of Cu_n nor that of NO_2. Therefore the NO_2 molecule is considered to be tightly bound to Cu_n in these cluster ions.

4 Conclusion

We have examined photoelectron spectra of the cluster anions, Cu_nN^-, Cu_nNO^-, and $Cu_nNO_2^-$, produced by the laser vaporization of Cu and by the reaction with NO. Especially for Cu_2N^-, coexistence of at least two isomers is concluded from the dependence on the expansion gas pressure. One of the isomers is considered to have a structure in which the central ion is Cu^- or Cu_2^- and the residual atom(s) are weakly bound to the ion. In the detachment of Cu_nNO^-, no electron signal was detected with photon energy of 3.49 eV. From this result and the recent results of the photoelectron spectroscopy of the CuO_2^- ion [18], the $CuNO^-$ ion is expected to have a structure in which the NO molecule dissociates and each atom is tightly bound to Cu.

From these studies it is recognized that higher photon energy for detachment is necessary in order to elucidate the electronic and geometrical structure of the cluster ions. We are now trying to utilize the fourth harmonic of the Nd:YAG laser (266 nm, 4.66 eV) for this experiment. Theoretical studies of both the neutral cluster and the cluster anions are also needed to explain the present results more rigorously. It is also planned in our laboratory to calculate the structures of diatomic and triatomic anions discussed in this paper.

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