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Dissociative photoionization of $Al_2(CH_3)_6$ and $Al_2(CH_3)_3Cl_3$ in the range 40–100 eV

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Dissociation processes of the organoaluminum compounds $Al_2(CH_3)_6$ and $Al_2(CH_3)_3Cl_3$ have been studied in the range of valence and Al:*2p* core-level ionization by means of photoelectron–photoion and photoion–photoion coincidence techniques. The double-ionization threshold and the Al:*2p* core-ionization threshold of $Al_2(CH_3)_6$ are estimated to be about 30 and 80 eV† respectively. The relative yields of the H^+–Al^+ and H^+–$CH_{m'}{}^+$ ($m'=0$–3) ion pairs are enhanced around the Al:*2p* core-ionization threshold of $Al_2(CH_3)_6$. The photoion–photoion coincidence intensities of $Al_2(CH_3)_3Cl_3$ are negligibly small throughout the energy range studied. The ratio of the relative yield of $AlC_2H_6^+$ to that of Al^+ increases smoothly through the Al:*2p* core-ionization and/or excitation region of $Al_2(CH_3)_3Cl_3$. The variation of the fragmentation pattern with photon energy is discussed in conjunction with the relevant electronic states.

Keywords: Organoaluminum, photoionization, synchrotron radiation

1 INTRODUCTION

Organometallic molecules containing aluminum atoms are important as source materials for metal- and compound-film growth by chemical vapor deposition. Recently, there has been a growing interest in light-stimulated chemical reactions in these molecular layers adsorbed on surfaces for direct writing of aluminum metalization on integrated circuits as well as for interconnect repair.[1-3] From the viewpoint of photochemical vapor deposition, it would be of great importance to study the photon energy dependence of the fragmentation pattern of the organometallic molecule containing aluminum atoms, especially to study the fragmentation pattern following Al:*2p* core excitation. Recently, the photofragmentation of organometallic molecules in the vacuum ultraviolet (VUV) and soft X-ray regions has been a topic of much interest.[4-14] In contrast to the case of valence electrons delocalized over the molecule, core electrons are localized near the atomic nucleus to which they belonged originally. As a result, photoexcitation from core orbitals is expected to produce dissociation pathways quite different from those following valence photoionization. Accordingly, we have initiated studies of core level photoionization and the subsequent fragmentation of organometallic molecules using synchrotron radiation.[4-13] Furthermore, it is interesting to study the processes following selective excitation of the same atomic core in different chemical environments in a molecule. Such site-specific excitation often results in different fragmentation patterns (site-specific fragmentation), owing to the localized nature of the core electron.[15-17] Site-specific fragmentation bears the possibility of being used as a technique for synthesizing new materials.

In the present study, we report dissociative ionization of $Al_2(CH_3)_6$ and $Al_2(CH_3)_3Cl_3$ in the energy range of valence and Al:*2p* core-photoionization. The Al:*2p* core-ionization threshold is expected to be about 80 eV [18, 19]. The variation of the fragmentation pattern with photon energy is discussed in conjunction with

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† 1 eV = 96.4853 kJ mol^{-1}.

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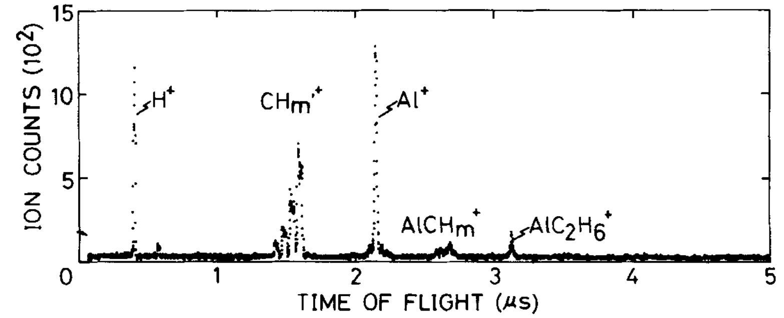

Figure 1 TOF mass spectrum of $Al_2(CH_3)_6$ taken by excitation at 81.3 eV in the PEPICO mode. Data collection time is 500 s, $m' = 0$–3, $m = 0$–4.

the relevant electronic states. Since $Al_2(CH_3)_3Cl_3$ has the structure $(CH_3)_2 \cdot Al \cdot Cl_2 \cdot Al \cdot Cl(CH_3)$,[20] and the chemical environments of the two aluminum atoms are different from each other, we try to examine whether or not the site-specific fragmentation is observed in $Al(CH_3)_3Cl_3$.

2 EXPERIMENTAL

The experiments were performed using a time-of-flight (TOF) spectrometer with variable path-length, coupled to a constant-deviation grazing incidence monochromator installed on the BL3A2 beam line of the UVSOR synchrotron radiation facility in Okazaki. The setup and the experimental procedures were described in detail in previous papers.[21,22] The TOF spectrometer can be operated in two different modes; a photoelectron–photoion coincidence (PEPICO) mode and a photoion–photoion coincidence (PIPICO) mode. A flight-path length of 20 cm was used in the present work. Thin film optical filters of beryllium, aluminum–tellurium, and tin were used for order sorting in the measurements in the regions 59–68 eV, 30–58 eV and 20–29 eV respectively. In the experiments with $Al_2(CH_3)_6$, the slit width of the monochromator was 0.5 mm, giving an optical resolution of 0.1 and 0.2 nm in the regions above and below 50 eV, respectively, whereas in the experiments with $Al_2(CH_3)_3Cl_3$ it was 0.4 mm, giving a corresponding resolution of 0.08 and 0.16 nm, respectively. The background pressure in the main chamber during operation was $(3–5) \times 10^{-7}$ Torr. $Al_2(CH_3)_6$ of 99.9999 % purity and $Al_2(CH_3)_3Cl_3$ were obtained from Rare Metallic and Aldrich, respectively, and were used without further purification.

3 RESULTS AND DISCUSSION

3.1 $Al_2(CH_3)_6$

Figure 1 shows an example of the TOF mass spectra of $Al_2(CH_3)_6$ taken in the PEPICO mode at 81.3 eV of photon energy. Although the main species existing in the vapor of $Al_2(CH_3)_6$ at room temperature is the dimer $[Al_2(CH_3)_6]$,[23–25] peaks corresponding to the dimer ions ($Al_2C_mH_n^+$, $m = 0$–6 and $n = 0$–18) were found to be extremely small throughout the energy range studied, just as in the case of the electron impact ionization of $Al_2(CH_3)_6$.[26] Each of the small ions, such as H^+, CH_3^+ etc., forms a doublet peak in the TOF mass spectra. The doublet structure indicates that the light fragments are emitted with large kinetic energies; some of these fragments with a large velocity component perpendicular to the TOF axis escape from the detection cone of the TOF spectrometer. Figures 2 and 3 show plots of the ratios of the integrated intensities of the various ion peaks in the TOF mass spectrum to the total photoion intensity ($I_{ion}/I_{tot\text{-}ion}$) as a function of photon energy.

Figure 4 shows an example of the PIPICO spectra of $Al_2(CH_3)_6$ taken at 81.3 eV of photon energy. Each of the ion pairs, e.g. CH_3^+–Al^+, forms a doublet peak in the PIPICO spectra, again owing to the kinetic energies released. Figures 5 and 6 show plots of the ratios of the integrated intensities of the various ion pairs in the PIPICO spectrum to the total double-photoionization ($I_{PIPICO}/I_{tot\text{-}PIPICO}$) as a function of photon energy. The double-photoionization threshold was estimated to be about 30 eV from the appearance energy of the PIPICO peaks.

The photon energy region below 80 eV is considered to correspond to that of the valence ionization of $Al_2(CH_3)_6$.[18,19] The variation of the fragmentation pattern with photon energy in this region can be explained in terms of the increase in the internal energy with increase of photon energy. It is shown that the fractions of the H^+ and $CH_{m'}^+$ ($m'=0$–3) ions are very small in the region below the double-photoionization threshold and increase when the photon energy is increased beyond the threshold. These facts indicate that the H^+ and $CH_{m'}$ species ($m'=0$–3) ions are mainly produced through dissociative double-photoionization and little from singly charged molecular ions.

From Figs 5 and 6, the overall fragmentation scheme of the doubly charged molecular ions of $AL_2(CH_3)_6$ in the region of the valence ionization may be described as shown in Scheme 1.

$Al_2(CH_3)_6 + h\nu$ (valence double-ionization)

$\rightarrow Al_2(CH_3)_6^{2+} + 2e$

$\rightarrow AlC_2H_6^+ + CH_3^+ + n.p.$

$\rightarrow AlCH_3^+ + CH_3^+ + n.p.$

$\rightarrow Al^+ + CH_{m'}^+ + n.p.$ ($m'=0$–3)

$\rightarrow Al^+ + H^+ + n.p.$

$\rightarrow H^+ + CH_m^+ + n.p.$ ($m'=0$–3)

Scheme 1 Abbreviations
n.p. denotes neutral products.

It is seen that both of the ratios $I_{ion}/I_{tot\text{-}ion}$ for the H^+ and $CH_{m'}^+$ ($m'=0$–3) ions and $I_{PIPICO}/I_{tot\text{-}PIPICO}$ for the H^+–Al^+ and $CH_{m'}^+$ ($m'=0$–3) ion pairs are enhanced around 80 eV. On the other hand, the ratios for the Al^+, $AlCH_3^+$ and $AlC_2H_6^+$ ions and the $CH_{m'}^+$–Al^+ ($m'=0$–3), CH_3^+–$AlCH_3^+$ and CH_3^+–$AlC_2H_6^+$ ion pairs are seen to decrease around 80 eV. Since the photon energy of 80 eV corresponds to that of the Al:2*p* core-ionization threshold,[18,19] these phenomena around 80 eV are considered to be due to Al:2*p* core-ionization and/or excitation.

As exemplified by the production of H^+–Al^+ and H^+–$CH_{m'}^+$ ($m'=0$–3) ion pairs, photoionization or photoexcitation from core orbitals enhances dissociation pathways different from those following valence photoionization. Core photoionization or photoexcitation is characterized by the localized nature of the electrons to be removed or excited, in addition to the large internal energy deposited in the ion produced. In contrast, the valence electrons are delocalized over the molecule. It is, therefore, not unexpected that the dynamic processes following core-ionization or excitation are quite different from those following valence-ionization.

It is believed that the major relaxation process following 2*p* ionization of free aluminum atom is the LMM Auger process which produces a doubly charged aluminum ion.[27] Assuming that a similar process plays a major role in the relaxation following 2*p* ionization of aluminum in $Al_2(CH_3)_6$ (LVV Auger process), the fragmentation scheme

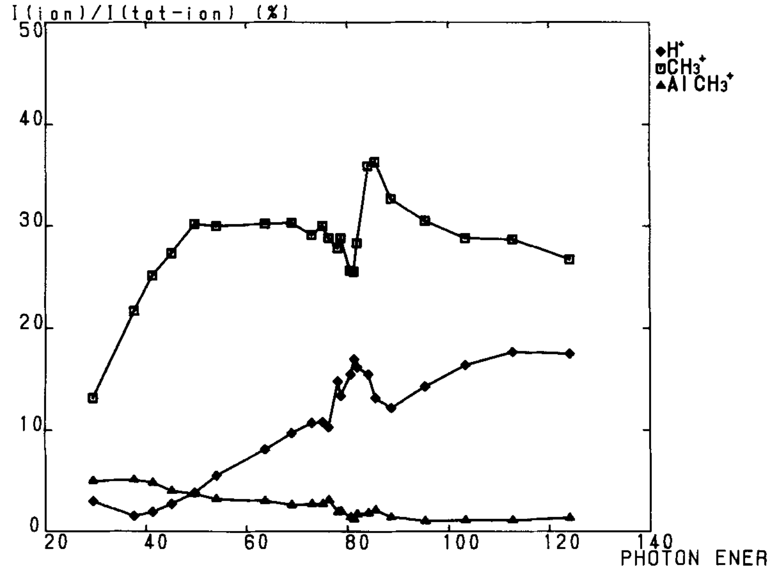

Figure 2 Ratios of integrated intensities of H^+, CH_3^+ and $AlCH_3^+$ ion peaks in TOF mass spectrum to total photoion intensity ($I_{ion}/I_{tot\text{-}ion}$) in $Al_2(CH_3)_6$ as a function of photon energy.

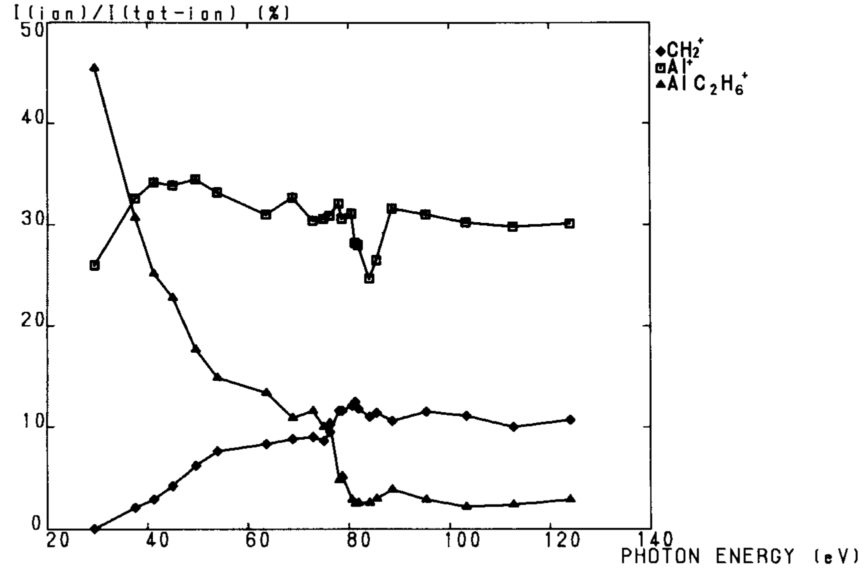

Figure 3 Ratios of integrated intensities of CH_2^+, Al^+ and $AlC_2H_6^+$ ion peaks in TOF mass spectrum to total photoion intensity ($I_{ion}/I_{tot\text{-}ion}$) in $Al_2(CH_3)_6$ as a function of photon energy.

leading to the production of the H^+–Al^+ and H^+–$CH_{m'}^+$ ($m'=0$–3) ion pairs in $Al_2(CH_3)_6$ may be described as shown in Scheme 2.

$Al_2(CH_3)_6 + h\nu$

$\rightarrow Al_2(CH_3)_6^+ + e$ (Al: 2*p* ionization)

$\rightarrow Al_2(CH_3)_6^{2+} + e$ (LV Auger)

$\rightarrow Al^+ + H^+ + \text{n.p.}$

$\rightarrow H^+ + CH_{m'}^+ + \text{n.p.}$ ($m'=0$–3)

Scheme 2

The H^+-Al^+ and H^+–$CH_{m'}^+$ ($m'=0$–3) ion pairs arise from the dissociation of the C–H bond. Thus, the production of these ion pairs following the Al: 2*p* core-ionization and the LVV Auger process might sound rather odd, because the C–H bonds lie apart from the aluminum atom. However, a similar type of fragmentation has been observed in acetone following O: 1*s* core excitation and a KVV Auger process;[28] CH_3^+ ion production is strongly associated with the excitation of an O: 1*s* electron. At present we do not have any plausible explanation for the above-mentioned production of the H^+–Al^+ and H^+–$CH_{m'}^+$ ($m'=0$–3) ion pairs following the Al: 2*p* ionization. Since the Auger transition is localized, the molecular orbitals that participate

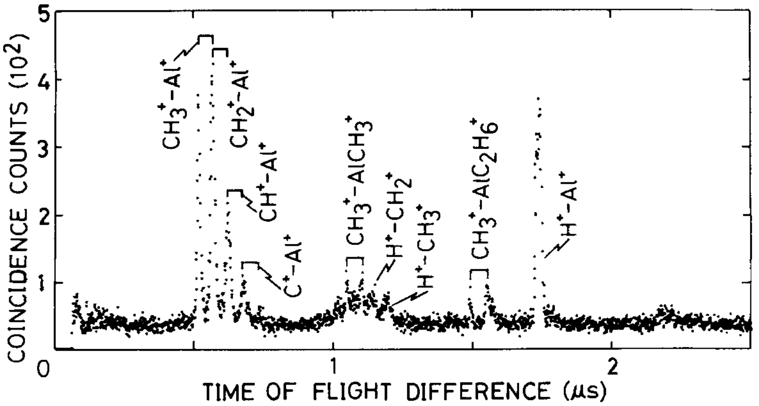

Figure 4 PIPICO spectrum of $Al_2(CH_3)_6$ taken by excitation at 81.3 eV. Data collection time is 1480 s.

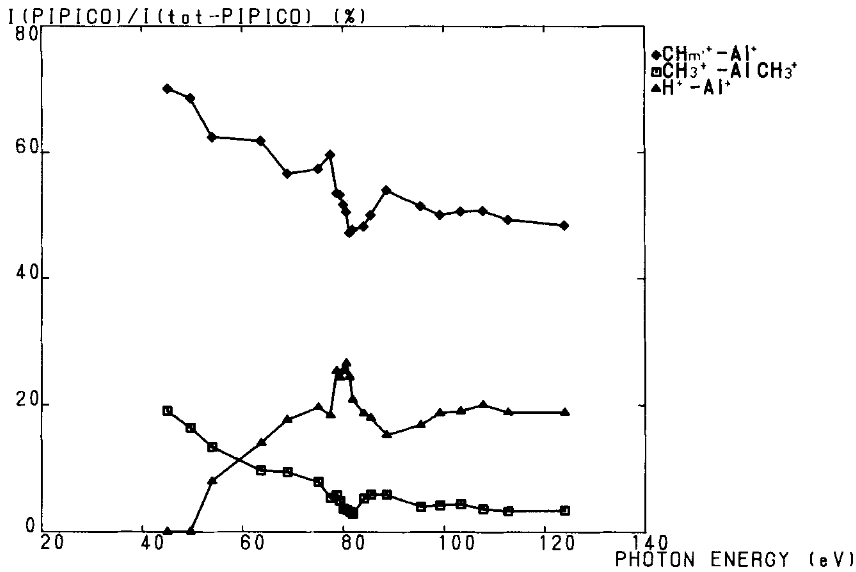

Figure 5 Ratios of integrated intensities of $CH_{m'}^+$–Al^+ ($m'=0$–3), CH_3^+–$AlCH_3^+$ and H^+–Al^+ ion pairs in PIPICO spectrum to total double-photoionization ($I_{\mathrm{PIPICO}}/I_{\mathrm{tot\text{-}PIPICO}}$) in $Al_2(CH_3)_6$ as a function of photon energy.

in the Auger decay would be those that have a large probability density on the atom with the core hole. The analysis of the overlap populations of the molecular orbitals reveals the contributions of these orbitals to the bonding structure of the molecule. Accordingly, the fact that the yields of H^+–Al^+ and H^+–$CH_{m'}^+$ ($m'=0$–3) are enhanced by Al: 2*p* ionization may be explicable by considering the molecular oritals and Auger transitions in $Al_2(CH_3)_6$. Although such an analysis has been used to interpret the fragmentation pattern in N_2O,[17] it is not immediately applicable to the case of $Al_2(CH_3)_6$, because necessary data are not available in the literature.

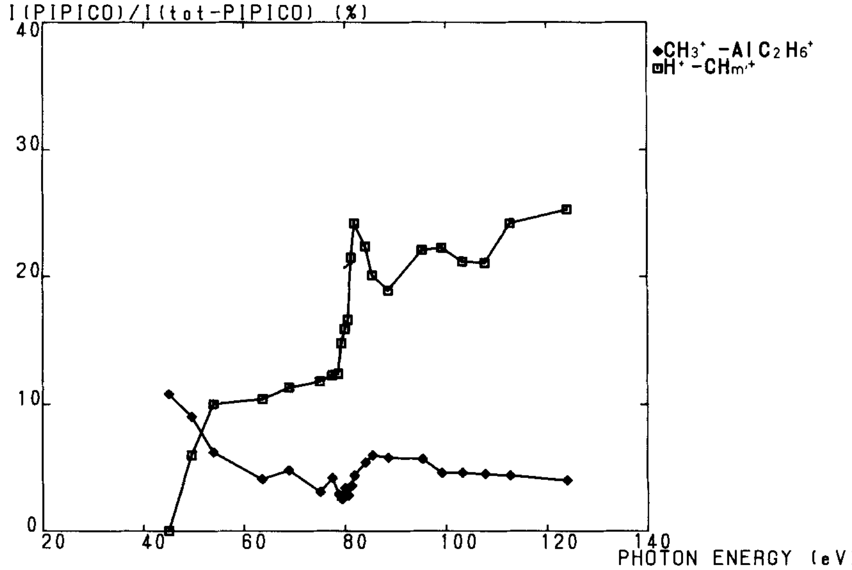

Figure 6 Ratios of integrated intensities of CH_3^+–$AlC_2H_6^+$ and H^+–$CH_{m'}^+$ ($m'=0$–3) ion pairs in PIPICO spectrum to total double-photoionization ($I_{\mathrm{PIPICO}}/I_{\mathrm{tot\text{-}PIPICO}}$) in $Al_2(CH_3)_6$ as a function of photon energy.

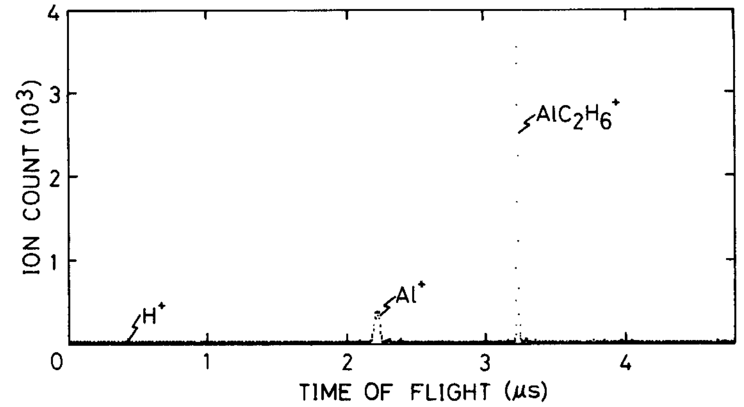

Figure 7 TOF mass spectrum of $Al_2(CH_3)_3Cl_3$ taken by excitation at 40 eV in the PEPICO mode. Data collection time is 1500 s.

3.2 $Al_2(CH_3)_3Cl_3$

Figure 7 shows an example of the TOF mass spectra of $Al_2(CH_3)_3Cl_3$ taken in the PEPICO mode at 40 eV of photon energy. Although the main species existing in the vapor of $Al_2(CH_3)_3Cl_3$ at room temperature is the dimer $Al_2(CH_3)_3Cl_3$,[20] the peaks corresponding to the dimer ions ($Al_2C_lH_mCl_n^+$, $l = 0$–3, $m = 0$–6 and $n = 0$–3) in the mass spectra were found to be negligibly small throughout the energy range studied, just as in the case of $Al_2(CH_3)_6$. Only three ions H^+, Al^+ and $AlC_2H_6^+$ were found in the mass spectra throughout the energy range studied (20–100 eV). The yield of H^+ was always very small.

Figure 8 shows plots of $I_{ion}/I_{tot\text{-}ion}$ for H^+, Al^+ and $AlC_2H_6^+$ as a function of photon energy. On the other hand, the PIPICO intensity was found to be unmeasurably weak for any possible ion-pair throughout the energy range studied. Actually we could not obtain PIPICO spectra within a reasonable time.

As the photon energy increases, $I_{ion}/I_{tot\text{-}ion}$ for Al^+ gradually increases in the range of 20–80 eV passes through a broad maximum around 80 eV and finally falls off in the range 80–100 eV (Fig. 8). The reverse is the case with $I_{ion}/I_{tot\text{-}ion}$ for $AlC_2H_6^+$ (Fig. 8). The increase and decrease of $I_{ion}/I_{tot\text{-}ion}$ for Al^+ and $AlC_2H_6^+$, respectively, with photon energy in the range 20–80 eV can be

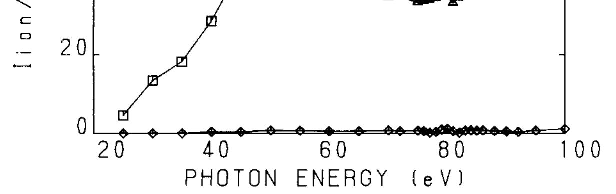

Figure 8 Ratios of integrated intensities of H^+, Al^+ and $AlC_2H_6^+$ ion peaks in TOF mass spectrum to total photoion intensity ($I_{ion}/I_{tot\text{-}ion}$) in $Al_2(CH_3)_3Cl_3$ as a function of photon energy.

explained in terms of the increase in internal energy with increase of photon energy. Similar results are generally obtained for the fragmentation patterns of various molecules following valence ionization.

However, an exception occurs in the range 80–100 eV in $Al_2(CH_3)_3Cl_3$ in which $I_{ion}/I_{tot\text{-}ion}$ for Al^+ decreases and that for $AlC_2H_6^+$ increases as the photon energy increases. Since the photon energy of 80 eV corresponds to that of the Al:2*p* core-ionization threshold as in the case of $Al_2(CH_3)_6$, this phenomenon is considered to be the consequence of the Al:2*p* core-ionization and/or excitation. At present, we cannot give an unambiguous explanation for this phenomenon, but the ionic and neutral fragments produced following Al:2*p* core-ionization and/or excitation of $Al_2(CH_3)_3Cl_3$ might be excited electronically, rotationally and/or vibrationally to a larger extent than those produced following valence ionization. Recently, we found that the effect of stray light of longer wavelengths is rather serious in the measurements at energies above 100 eV owing to the incomplete optical system of the beam line. Whether or not such an effect also exists in the above results obtained below 100 eV is under examination.

As mentioned above, the PIPICO intensities of $Al_2(CH_3)_3Cl_3$ were found to be negligibly small throughout the energy range studied. Moreover, the mass spectra show that stable doubly-charged parent ions of $Al_2(CH_3)_3Cl_3$ do not exist either. This might indicate that, distinct from the case of almost all other molecules including $Al_2(CH_3)_6$, double ionization does not take place in $Al_2(CH_3)_3Cl_3$ to any noticeable extent in the above energy range, although it should certainly be possible energetically. This, however, is an unbelievable interpretation, since it would mean that the LVV Auger process does not take place following the Al:2*p* ionization in $Al_2(CH_3)_3Cl_3$. A more plausible interpretation would then be that the doubly-charged molecular ions of $Al_2(CH_3)_3Cl_3$ exclusively dissociate into $Al^+ + Al^+ +$ n.p., regardless whether they are produced by direct double ionization of valence electrons or through LVV Auger. In this case, the PIPICO signal would not have been observed with our apparatus because of the almost zero TOF difference between the two Al^+ moieties, viz. a time difference which is smaller than the time resolution of the time-to-pulse height converter used.

In Fig. 7, it can be seen that the width of the Al^+ peak is broader than that of the $AlC_2H_6^+$ peak. This could be evidence for the above interpretation, including that the Al^+ ions were produced, at this photon energy, with a large kinetic energy due to Coulomb explosion of the doubly-charged ions. We naturally wanted to compare the Al^+ peak widths between the TOF mass spectra taken at energies below and above the double ionization threshold. Unfortunately, however, the intensities of the Al^+ ions in the energy region below the threshold were too weak to allow this comparison.

In any event, this system offers a striking contrast with $Al_2(CH_3)_2$ in that fragment ions of the type $CH_{m'}^+$ ($m' = 0\text{–}3$) are not formed at all. The main structural difference between $Al_2(CH_3)_3Cl_3$ and $Al_2(CH_3)_6$ in the vapor phase is that the two methyl groups bridging two aluminum atoms in the $Al_2(CH_3)_6$ dimer are replaced by two chlorine atoms in $Al_2(CH_3)_3Cl_3$.[20] Thus, the above fact may indicate that the CH_{m}^+ fragment ions in $Al_2(CH_3)_6$ originate from the central (bridging) methyl groups and not from the terminal methyl groups. It can also be noted in Figs 2, 3, 5 and 6 that the prominent changes in the relative ion yield curves or the relative PIPICO yield curves of $Al_2(CH_3)_6$ at the Al:2*p* threshold are mostly related to the $CH_{m'}^+$ and H^+ ions (i.e. to the methyl group), whereas no conspicuous changes in the ion yields (Al^+ and $AlC_2H_6^+$) are observed in $Al_2(CH_3)_3Cl_3$ at the Al:2*p* threshold. From all these facts, it may be concluded that the effect of the Al:2*p* ionization in these compounds is primarily exerted on the central (bridging) atom adjacent to the aluminum atom. The absence of the methyl group (a group of atoms that can be further dissociated differently depending on the energy partitioned) in this central position may be the reason for the absence of the conspicuous change in $Al_2(CH_3)_3Cl_3$ at the Al:2*p* threshold. The absence of the peaks corresponding to Cl^+ ions in the mass spectra of $Al_2(CH_3)_3Cl_3$ might then be related to the much higher ionization potential of chlorine (12.97 eV, [29, 30]) than that of CH_3 (9.840 eV)[31–33] and/or the difference in the bond energies between the Al–C–Al and Al–Cl–Al bonds (halogen bridging is known to be stronger than allyl bridging in these compounds).

In the present study, we could not observe any site-specific behavior in the fragmentation pattern of $Al_2(CH_3)Cl_3$ around the Al:2*p* core-ionization threshold. The reason for this may be that the energy resolution was not sufficient in the present experiment and/or that the difference in chemical environment between the two aluminum atoms in $Al_2(CH_3)_3Cl_3$ is not so drastic as to cause a sufficient chemical shift difference of the $2p$ ionization energy. Further investigation with higher resolution is clearly needed.

4 CONCLUSION

Dissociation processes of $Al_2(CH_3)_6$ and $Al_2(CH_3)_3Cl_3$ have been studied in the range of valence and Al:$2p$ core-level ionization by means of the PEPICO and PIPICO methods. The double-ionization threshold and the Al:$2p$ core-ionization threshold of $Al_2(CH_3)_6$ are estimated to be about 30 and 80 eV, respectively. The relative yields of the H^+–Al^+ and H^+–$CH_{m'}^+$ ($m' = 0$–3) ion pairs are enhanced around the Al:$2p$ core-ionization threshold of $Al_2(CH_3)_6$. The PIPICO intensities of $Al_2(CH_3)_3Cl_3$ are negligibly small throughout the energy range studied. The ratio of the relative yield of $AlC_2H_6^+$ to that of Al^+ increases smoothly through the Al:$2p$ core-ionization and/or excitation region of $Al_2(CH_3)_3Cl_3$.

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