Production of Pb^+ Ions Following 5*d* Core Photoionization of Tetramethyl Lead as Revealed by a Coincidence Experiment

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Ionic fragmentation following Pb 5*d* core-level ionization in tetramethyl lead ($PbMe_4$) has been studied with synchrotron radiation. In the wavelength range between 45 and 75 nm, photoionization of the Pb 5*d* core levels is observed in the threshold electron spectrum of $PbMe_4$. The efficiency for the production of Pb^+ ions increases dramatically in this region, while those of other fragment ions decrease. It is shown that the Pb^+ ion is predominantly produced following 5*d* photoionization by use of the threshold-electron–photoion coincidence technique.

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Shallow-valence-level ionization and the subsequent fragmentation of molecules have been studied extensively with the use of various kinds of light sources in recent years. However, the investigation of processes following core-level excitation has not been as extensive, because, for the purpose of such investigation, the conventional light sources are insufficient in both photon energy and intensity. Very recently, synchrotron radiation (SR) has provided a powerful means to obtain information about the core-level excitation, and the dynamic processes following core-level excitation in molecules are forming a research field of current interest.[1-6]

In contrast to the case of the valence electrons delocalized over the molecule, the core electrons in a molecule are localized near the atom to which they originally belonged. As a result, the photoionization of the core level is expected to produce dissociation pathways quite different from those following valence photoionization. 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.[1,3]

Volatile compounds with group-IV elements are particularly suitable for detailed investigations of the above-mentioned process in the vapor phase because of the rather small binding energies of the $(n-1)d$ core electrons. We have initiated studies of the core-level photoionization and subsequent fragmentation in such compounds.[7]

In photoionization, any amount of excess energy can be removed as kinetic energy of the ejected electron. Accordingly, upon irradiation at the threshold wavelength for a core-ionized state, various ionic states lying lower than this state are also produced. Thus, from the observation of photodissociation products alone, only indirect information is obtained on the processes induced by core ionization. In order to observe the dissociation processes following core-level ionization selectively, it is desirable to use the threshold-electron–photoion coincidence (TEPICO) method.[8-10] Since threshold electrons at a fixed wavelength correspond to the formation of ions with the highest internal energy attainable with that wavelength, the TEPICO measurements allow selective observation of processes initiated by those ions. In the present study, we have determined, by use of TEPICO, the relative efficiency for the production of fragment ions $Pb(CH_3)_3{}^+$, $Pb(CH_3)_2{}^+$, $PbCH_3{}^+$, and Pb^+ from various states of the tetramethyl-lead ($PbMe_4$) parent ion. Emphasis is placed on the Pb^+ ion, which seems to be produced predominantly following Pb 5*d* photoionization.

The experiments were performed with the TEPICO-II apparatus[7,11] installed in the BL3B beam line of the UV-SOR SR facility in Okazaki. The setup and the experimental procedures for the TEPICO measurements have been described in detail elsewhere.[7,11] Briefly, the ions and photoelectrons produced with monochromatic SR are repelled from the ionization region in opposite directions. The mass-analyzed ion signals for each fragment ion are then counted in coincidence with the threshold-electron signals obtained with a steradiancy threshold-electron analyzer. $PbMe_4$ vapor at room temperature was introduced into the ionization region as a continuous supersonic jet. The background pressure in the main chamber during operation was about 1×10^{-5} mbar. The experimental data were corrected for the spectral intensity of the exciting light. The wavelength reading was calibrated with respect to the threshold-electron spectra of Ne and Ar. The slit width of the 3-m normal-incidence monochromator[12] was typically 0.2 mm, giving a resolution of the incident light of about 0.02 nm. In order to obtain sufficient intensities for all fragment ions, the quadrupole mass spectrometer was used with a reduced resolution such that each of the fragment ions Pb^+, $PbCH_3{}^+$, $Pb(CH_3)_2{}^+$, and $Pb(CH_3)_3{}^+$ forms a broad single peak without resolution of the individual isotopes of Pb in each group. The photoionization-efficiency curves and the TEPICO spectra were taken by our fixing m/e at the highest intensity position in each broad peak. The resolution of the electron analyzer was about 30 meV.[7,11] $PbMe_4$ obtained from Rare Metallic was used without further purification.

$PbMe_4$ has the following electronic configuration (T_d point-group symmetry): Pb 5*d* core orbitals,

$$e^4t_2^6;$$

valence molecular orbitals,

$$1t_2^6 1a_1^2 1e^4 2t_2^6 1t_1^6 2a_1^2 3t_2^6.$$

Energies of the outer valence orbitals ($1a_1$–$3t_2$) have been measured by He I photoelectron spectroscopy,[13,14] but none are reported on the inner valence ($1t_2$) and core orbitals.

Figure 1 shows the threshold-electron spectrum of $PbMe_4$ in the region 40–90 nm. Several sharp bands are seen in the region 45–75 nm, while a broad huge peak occurs above 75 nm. The energies of the sharp peaks are close to the binding energies of the $5d_{3/2}$ and $5d_{5/2}$ electrons of the Pb free atom (28.23 and 25.27 eV, respectively).[15] Although neither the core nor the $1t_2$ valence bands have been observed so far,[13,14] the widths of valence bands are expected to be much larger than those observed in the region 45–75 nm in Fig. 1.[13,14] The $1t_2$ band is considered to be hidden in the other valence bands. Thus we temporarily assign these sharp bands to the photoionization of the Pb 5*d* core orbitals which are shifted to the red and split from those of atomic Pb. The problem of this assignment is further discussed later, although we cannot reach an unambiguous conclusion at present because of the lack of spectroscopic data in this wavelength range. Nevertheless, we have performed the ion-fragmentation experiments at wavelengths corresponding to some of these sharp peaks, as well as those belonging to the broad-band region.

Figure 2 shows the photoionization-efficiency curves for fragment ions from $PbMe_4$. The abundance of the parent ion $[Pb(CH_3)_4{}^+]$ was found to be extremely small throughout the wavelength range studied, just as in the case of electron-impact ionization of $PbMe_4$.[16] A striking feature in Fig. 2 is that the photoionization-efficiency curve for the Pb^+ ion has an appearance quite different from those for other fragments: The yield of the Pb^+ ion dramatically increases below the wavelength which we consider to correspond to the 5*d* onset, while those of other ions decrease. Moreover, almost all peaks of the Pb^+ curve in the region 45–75 nm are found to coincide in position with those in the threshold-electron spectrum (Fig. 1). These facts strongly suggest that the production of the Pb^+ ions predominantly occurs through excitation to the electronic states of the parent ion that correspond to the sharp peaks in the threshold-electron spectrum, in distinction from the other fragment ions which seem to originate from parent-ion states corresponding to the broad band.

In order to confirm these points, we have measured the TEPICO spectra for all fragment ions from $PbMe_4$. The ions measured in coincidence with threshold electrons at a fixed wavelength strictly represent those originating from the parent ions with the highest internal energy attainable with that wavelength. Figure 3 shows an example of the time-of-flight coincidence spectrum for Pb^+

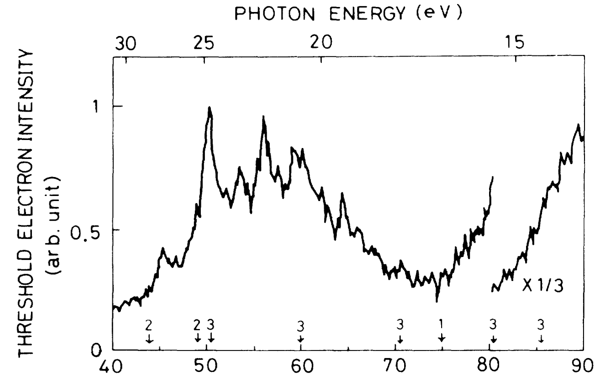

FIG. 1. Threshold-electron spectrum of $PbMe_4$ in the range 40–90 nm. 1, 2, and 3 indicate the positions of the assumed 5*d* onset, Pb atomic lines, and the TEPICO measurements, respectively.

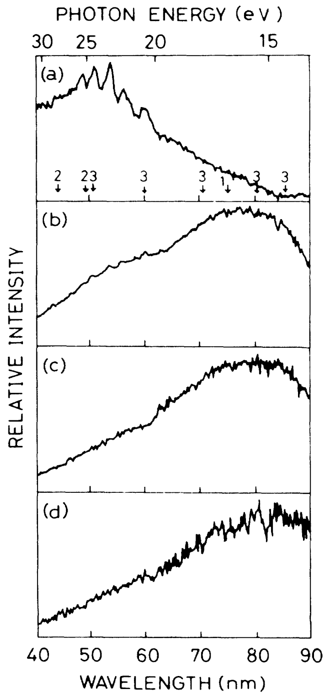

FIG. 2. Photoion-efficiency curves for (a) Pb^+, (b) $Pb(CH_3)^+$, (c) $Pb(CH_3)_2{}^+$, and (d) $Pb(CH_3)_3{}^+$ from $PbMe_4$ in the range 40–90 nm. 1, 2, and 3 indicate the positions of the assumed 5*d* onset, Pb atomic lines, and the TEPICO measurements, respectively.

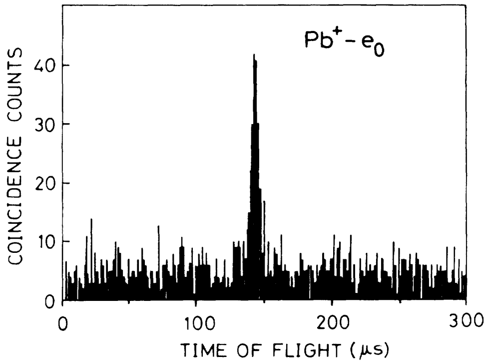

FIG. 3. Time-of-flight TEPICO spectrum of the Pb^+ ion taken with excitation at 50.4 nm. Data-collection time is 100 min.

taken at 50.4 nm, which belongs to the sharp-band region of the threshold-electron spectrum. It is seen that a sufficiently high signal-to-noise ratio is attained with reasonable data-collection time, illustrating the practicability of the TEPICO experiments. Similar coincidence peaks were obtained for Pb^+ at another wavelength belonging to the same region (60.0 nm), but were hardly obtained at wavelengths corresponding to the broadband region (above about 70 nm). On the other hand, the coincidence peaks for other fragment ions were easily obtained at the latter wavelengths, while they were not at 50.4 and 60.0 nm. This conclusively supports the above view suggested by the appearance of the photoionization-efficiency curves.

From the integrated intensities of the TEPICO peaks for the individual fragments, relative efficiencies of various ionic states for the production of each fragment were determined at 50.4, 60.0, 70.4, 80.4, and 85.4 nm. The relative efficiencies were obtained by our dividing the coincidence-peak intensities for a given data-collection time by the threshold-electron counting rates; i.e., the efficiency represents the number of each fragment ion obtained per unit number of the relevant parent ions produced. The results are summarized in Fig. 4. Error bars indicate uncertainties of the determination, mainly coming from statistical errors. The TEPICO signals were negligible for $Pb(CH_3)_2^+$ at 50.4 and 60.0 nm and for $Pb(CH_3)_3^+$ at 50.4, 60.0, 70.4, and 80.4 nm.

Several interesting features are immediately evident from Fig. 4. Below about 70 nm, the efficiency for the production of Pb^+ ions increases sharply, and Pb^+ is by far the most abundant fragment ion. Above about 70 nm, on the other hand, the production of other fragments is enhanced considerably, and the efficiency for Pb^+ production quickly goes down.

Now the question is as follows: What are the ionic states corresponding to the sharp bands in the 45–75-nm range of the threshold-electron spectrum? As mentioned above, no spectroscopic data exist for this compound in this wavelength range. Since our coincidence experiments have indubitably demonstrated that these states dissociate into fragments in a manner quite different from that of the ionic states associated with the intense broadband of the threshold-electron (valence-ionized states), we must consider these states to be of fundamentally different nature from the valence-ionized states. Thus, at present we temporarily assign these states to the Pb 5*d* core-ionized states. Although the onsets for the $5d_{5/2}$ and $5d_{3/2}$ core ionization of the free Pb atom occur at 49.1 nm (25.3 eV) and 43.9 nm (28.2 eV), respectively,[15] these are considered to be shifted to the red in the methyl compound. In fact, such a red shift has been observed in the He II photoelectron spectrum of tetraethyl lead.[17] The $5d^9$ hole states are split as a result of both the spin-orbit coupling and the electrostatic perturbation from the methyl groups. These irregularly split $5d^9$ hole states seem to be responsible for the sharp peaks of the threshold-electron spectrum.

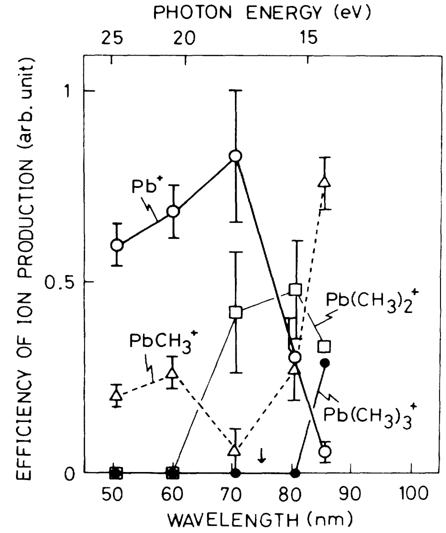

FIG. 4. State-selected efficiency of ion production for Pb^+ (open circles), $PbCH_3^+$ (triangles), $Pb(CH_3)_2^+$ (squares), and $Pb(CH_3)_3^+$ (closed circles). The arrow indicates the position of the assumed 5*d* onset.

In the absorption spectrum of the free Pb atom,[18] the peaks observed in the 45.0–70.0-nm range are assigned to the 5*d*-6*p* resonances, followed by autoionization resulting in the formation of various 6*p*- and 6*s*-ionized states.[19] In the present case, however, the possibility of such autoionization producing lower-lying valence-ionized states is excluded because what we measure is the threshold electrons. A threshold electron through autoionization means that the ionic state produced is energetically in resonance with the autoionizing state. Such an ionic state cannot be a valence-ionized state, since it is unlikely that discrete vibrational states of a valence-ionized state persist up to such high energies. Thus, even if the sharp peaks in question originate from autoionization, the ionic states produced must be $5d$-ionized states in all probability. However, at present we believe that these peaks are due mostly to direct ionization rather than autoionization, since it is also unlikely that an autoionizing state is accidentally in resonance with all these ionic states.

From these considerations, we assign the sharp peaks in the threshold-electron spectrum to the $5d$ core-ionized states, and interpret the observed fragmentation pattern in this region, different from that in the longer-wavelength region, as due to the core ionization.

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[1] W. Eberhardt, T. K. Sham, R. Carr, S. Krummacher, M. Strongin, S. L. Weng, and D. Wesner, Phys. Rev. Lett. **50**, 1038 (1983).

[2] W. Eberhardt, J. Stöhr, J. Feldhaus, E. W. Plummer, and F. Sette, Phys. Rev. Lett. **51**, 2370 (1983).

[3] K. Müller-Dethlefs, M. Sander, L. A. Chewter, and E. W. Schlag, J. Phys. Chem. **88**, 6098 (1984).

[4] P. Morin, G. G. B. de Souza, I. Nenner, and P. Lablanquie, Phys. Rev. Lett. **56**, 131 (1986).

[5] G. Dujardin, L. Heller, D. Winkoun, and M. J. Besnard, Chem. Phys. **105**, 291 (1986).

[6] P. Morin and I. Nenner, Phys. Rev. Lett. **56**, 1913 (1986).

[7] S. Suzuki, S. Nagaoka, I. Koyano, K. Tanaka, and T. Kato, Z. Phys. D **4**, 111 (1986).

[8] K. Tanaka and I. Koyano, J. Chem. Phys. **69**, 3422 (1978); I. Koyano and K. Tanaka, J. Chem. Phys. **72**, 4858 (1980).

[9] I. Nenner, P.-M. Guyon, T. Baer, and T. R. Govers, J. Chem. Phys. **72**, 6587 (1980).

[10] K. Tanaka, T. Kato, P. M. Guyon, and I. Koyano, J. Chem. Phys. **79**, 4302 (1983), and references therein.

[11] I. Koyano, K. Tanaka, T. Kato, S. Suzuki, and E. Ishiguro, Nucl. Instrum. Methods Phys. Res., Sect. A **246**, 507 (1986).

[12] M. Itou, T. Harada, T. Kita, K. Hasumi, I. Koyano, and K. Tanaka, Appl. Opt. **25**, 2240 (1986).

[13] S. Evans, J. C. Green, P. J. Joachim, A. F. Orchard, D. W. Turner, and J. P. Maier, J. Chem. Soc. Faraday Trans. 2 **68**, 905 (1972).

[14] A. E. Jonas, G. K. Schweitzer, F. A. Grimm, and T. A. Carlson, J. Electron Spectrosc. Relat. Phenom. **1**, 29 (1972/1973).

[15] N. Sander, V. Schmidt, W. Mehlhorn, F. Wuilleumier, M. Y. Adam, and J. P. Desclaux, J. Phys. B **13**, 2937 (1980).

[16] B. G. Hobrock and R. W. Kiser, J. Phys. Chem. **65**, 2186 (1961).

[17] G. M. Bancroft, L. L. Coatsworth, D. K. Crebar, and J. Tse, Chem. Phys. Lett. **50**, 228 (1977), and Phys. Scr. **16**, 217 (1977).

[18] J. P. Connerade, W. R. S. Garton, M. W. D. Mansfield, and M. A. P. Martin, Proc. Roy. Soc. London, Ser. A **357**, 499 (1977).

[19] M. O. Krause, A. Svensson, A. Fahlman, T. A. Carlson, and F. Cerrina, Z. Phys. D **2**, 327 (1986).