PHYSICAL REVIEW A **82**, 045401 (2010)

Projection of excited orbitals into kinetic energies of emitted electrons in resonant Si KLL Auger decays of SiF_4

I. H. Suzuki,[1,*] Y. Kono,[2] A. Ikeda,[2] T. Ouchi,[3] K. Ueda,[3] O. Takahashi,[4] I. Higuchi,[5] Y. Tamenori,[5] and S. Nagaoka[2]
[1]*Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba 305-0801, Japan*
[2]*Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790-8577, Japan*
[3]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan*
[4]*Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*
[5]*Japan Synchrotron Radiation Research Institute/SPring-8, 1-1-1 Kouto, Sayo-cho, Sayo-gun 679-5198, Japan*
(Received 25 June 2010; published 6 October 2010)

Spectator resonant Auger-electron spectra have been measured in the Si 1s photoexcitation region of SiF_4 using an electron spectroscopic technique combined with undulator radiation. A transition with the highest intensity in the total ion yield spectrum, which comes from excitation of a 1s electron into the 6t_2 valence orbital, generates resonant Auger decays in which the excited electron remains predominantly in the valence orbital or is partly shaken up into a high-lying Rydberg orbital. The higher-lying peak generated through excitation into Rydberg orbitals induces resonant Auger decays in which the excited Rydberg electron is partly shaken up to a higher-lying Rydberg orbital or shaken down to a lower-lying valence molecular orbital. These findings exhibit a clear disentanglement effect among excited orbitals which are smeared out in the 1s electron excitation spectrum.

DOI: 10.1103/PhysRevA.82.045401 PACS number(s): 32.80.Hd, 33.20.Rm, 33.60.+q, 33.80.Eh

I. INTRODUCTION

Inner-shell excitation spectra of small molecules clarify characteristics of molecular orbitals unoccupied in the ground state, which are often unclear in photoabsorption spectra in the region of valence orbital excitation. The spectra related to shallow inner shells provide clear evidence of the assignments of the excited orbitals [1]. However, with an increase in excitation energy, photoabsorption peaks exhibit complex structures due to an increase in lifetime width and due to experimental difficulties in energy resolution. K-shell excitation spectra of Si-containing molecules were measured using synchrotron radiation by Bodeur and co-workers and showed wide peak structures overlapping one another below ionization thresholds [2]. They proposed assignments to those peaks, which agreed with those calculated by the *ab initio* configuration-interaction technique. However, their calculated relative intensities did not agree with measured intensities for SiF_4. Recent studies using the density-functional theory (DFT) well reproduced the experimental excitation spectra for several molecules [3]. The Si 1s excitation spectrum of SiF_4 has been calculated within the framework of DFT, which indicated agreement with that observed recently [4].

On the other hand, inner-shell ionization in the soft-x-ray region usually induces Auger-electron emission because of the low probability of radiative processes. In the photoexcitation of an inner-shell electron into a vacant orbital, resonant Auger electrons emerge [5–10]. The final state in a spectator-type process is represented by a spectator electron and a doubly charged ion core, which is assumed to be the same as the state in the normal Auger (NA) decay. In rare gas atoms, this spectator electron has been investigated in detail in many instances; the electron was found to remain in a state with the same principal quantum number, or to be shaken up to a state with a different quantum number [9,10]. Resonant Auger decays have been studied for many molecules that usually exhibit complex structures due to vibrational mode and densely located valence holes. These findings make it very difficult to conduct a precise analysis of the final states. Resonant Si LVV Auger decays were studied for SiF_4 by several groups [5–8]. The observed spectra indicated the energy shifts of the broad peak structures to higher kinetic energies and lower binding energies, than those of NA decays and those shifts depended on the excitation photon energy. However, a sharp peak structure was not found and the behavior of the spectator electrons during LVV Auger decays was not pursued.

KLL Auger-electron spectra of Si compounds were observed using an electron beam technique by Kelfve and colleagues [11]. Those spectra showed relatively simple characteristics in the KLL decays owing to a near-atomic process of Auger decays between inner shells and then they clearly analyzed chemical shifts among many molecules on the basis of calculated results using relatively simple theories. The Si 1s photoelectron spectrum of SiF_4 exhibits a simple peak structure by limited movement of the Si atom, which essentially shows no vibrational excitation [4]. These results suggest that monochromatic photoexcitation of Si-containing molecules yields a simple spectrum for resonant Auger transitions from Si K-shell excited states. Our previous study using the $F_3SiC_2H_4Si(CH_3)_3$ molecule indicated that some photoexcited states of Si 1s electrons decomposed into different states of singly charged ions with two 2p holes during resonant Auger decays [12]. This decomposition yielded a spectator electron existing in some Rydberg orbitals and/or valence molecular orbitals. In order to clarify the behavior of spectator electrons, it is important to measure the resonant KLL Auger-electron spectra of SiF_4 precisely.

In the present study, resonant Auger electrons of the spectator type induced through Si 1s excitation have been observed using monochromatized undulator radiation and a hemispherical electron energy analyzer. The observed electron

---

[*] Corresponding author: suzukii@post.kek.jp

kinetic energy spectra ranging from 1583 eV to 1617 eV have shown final state configurations consisting of two $2p$ holes and of a Rydberg electron or valence electron. Rydberg electrons are found to be shaken up and shaken down and a varying behavior is found for excited valence electrons.

II. EXPERIMENT

Measurements were performed on the c branch of the soft-x-ray photochemistry beamline BL27SU at the SPring-8 facility [13]. The energy calibration of the monochromator was performed using the Ne 1s photoelectrons [14]. The photon bandwidth employed was about 0.53 eV in most instances. The intensity of the monochromatized incident photon beam during the measurement was monitored by collecting the drain current of the postfocusing mirror in the beamline. An electron spectrometer used consists of a hemispherical electron spectrometer (Gammadata Scienta, SES-2002) fitted to a gas cell (GC-50) by way of a multielement lens in a differentially pumped chamber [10]. Sample gas of SiF_4 was supplied into the gas cell and the gas density observed in the chamber during the measurements was 2×10^{-4} Pa. The energy width of the electron spectra was estimated to be 0.47 eV. The electron energy was calibrated using the peak energies for the Auger decay from the Ne K-shell hole state [15].

III. RESULTS AND DISCUSSION

Figure 1 shows electron emission spectra in the direction parallel to the photon polarization at several photon energies (1846.1, 1848.5, 1849.9, and 1951.6 eV) in the Si 1s excitation region as a function of electron kinetic energy. Peak structures are designated with labels such as V_1, R, and shake-up, which are explained below with reference to a two-dimensional map of electron signals (2D map). Figure 1(a), measured at 1951.6 eV, exhibits normal Auger lines of Si $KL_{23}L_{23}$. These peaks are assigned to ${}^1D_2$ for the electron kinetic energy of 1595.3 eV, to ${}^1S_0$ at 1588.9 eV, and to a satellite at 1587.5 eV, in the atomic representation. The present energy values are in good agreement with the data previously reported by Kelfve *et al.* [11]. In Fig. 1(b), three peaks with high intensities are found. The three peaks originate from resonant Auger decays into final states with the core hole of ${}^1D_2$ and with an excited spectator electron. Figure 1(c), which exhibits the spectrum measured at the highest peak of a total ion yield (TIY) spectrum, shows a high peak at 1605.1 eV and a peak at 1598.5 eV. The higher peak, named V_2, comes from the spectator Auger decays following 1s excitation into the vacant valence orbital, $6t_2$. The spectrum in Fig. 1(d) shows a peak at 1604.9 eV, coming from the resonant Auger decay into the state with the ${}^1D_2$ hole and $6a_1$ spectator electron. Each of the electron spectra exhibited in Fig. 1 corresponds to a plot of electron signals along a horizontal line on the 2D map shown in Fig. 2.

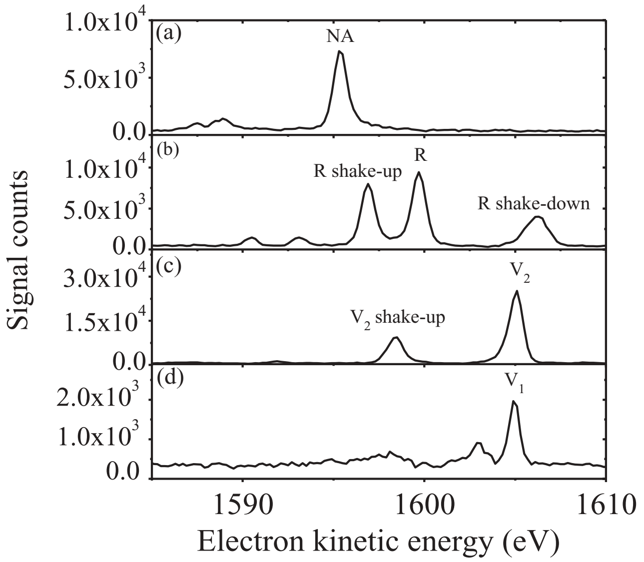

FIG. 1. Electron emission spectra at several photon energies near the Si 1s ionization thresholds in the electron energy region from 1585 eV to 1610 eV. (a) 1951.6 eV (normal Auger-electron spectrum), (b) 1849.9 eV, (c) 1848.5 eV, and (d) 1846.1 eV. See the text for an explanation of labels such as R, V_1, and V_2 shake-up. NA denotes peaks of normal Auger electrons.

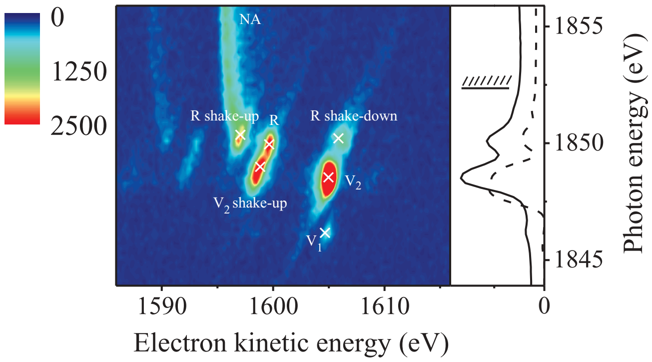

FIG. 2. (Color online) Two-dimensional map of emitted electron signals in the Si $KL_{23}L_{23}$ region. The total ion yield (TIY) spectrum is displayed at the right end, together with a calculated spectrum. The hatched bar in the TIY denotes the ionization threshold of the Si 1s electron. See the text for an explanation of labels such as R, V_1, and V_2 shake-up.

Figure 2 shows the 2D mapping of Auger-electron emission under the parallel photon polarization in the transition region of Si $1s^{-1}v*$ states into Si $2p^{-2}v*$ states, where $v*$ denotes a vacant molecular orbital and/or a Rydberg-type orbital. The abscissa denotes the electron energy and the ordinate indicates the photon energy for Si 1s excitation. The labels and structures of this figure are explained below. The photoexcitation spectra are shown at the right end of the figure, where the solid curve represents a measured TIY spectrum, the broken one indicates a calculated photoexcitation, and the ionization energy of the Si 1s electron is shown with a hatched bar. The TIY clearly shows two resonance peaks at 1848.5 and 1849.9 eV and a tiny peak at 1846.1 eV [4]. These peaks have been ascribed to excitation of the Si 1s electron into the $6t_2$ valence molecular orbital, $7t_2$ valence orbital coupled with 4p Rydberg orbital, and $6a_1$ orbital, respectively. In the 2D map can be seen a long vertical island at a kinetic energy of about 1595 eV, the label NA, and six islands with high intensities at several kinetic energies. The long vertical island comes from the normal Auger peak of the $^1D_2$ core hole and is slightly bent because the postcollision interaction has some effect on the energy of NA decay.

The low-intensity island, V_1, is found at the photon energy of 1846.1 eV and the electron kinetic energy of 1604.8 eV. This island is connected with the lowest-energy peak in the TIY spectrum, which is assigned to the transition to the $6a_1$ orbital, originating from deformed structures by vibrational motion [4]. The highest-intensity island, V_2, is seen around the photon energy of 1848.5 eV and the electron energy of 1605.1 eV. The Si 1s excited state at this photon energy is presumed to decay into the Si $2p^{-2}$:$^1D_2$ ($6t_2$) state mainly in the following way:

$$M + h\nu \rightarrow M^*(\mathrm{Si}\ 1s^{-1}\,6t_2) \rightarrow M^+(\mathrm{Si}\,2p^{-2} : {}^1D_2\,6t_2) + e. \tag{1}$$

In this scheme, M denotes the SiF$_4$ molecule.

The island with the second highest intensity, theV_2 shake-up, is yielded by the resonant Auger decay into the state having an electron in a higher-lying orbital as well as the core hole of $^1D_2$ at the same photon energy as the island V_2. This process is represented by the following scheme, where the orbital is indicated using a Rydberg orbital with a principal quantum number n':

$$M + h\nu \rightarrow M^*(\mathrm{Si}\ 1s^{-1}6t_2) \rightarrow M^+(\mathrm{Si}\ 2p^2 : {}^1D_2\ n'l') + e \tag{2}$$

Table I lists the characteristics of island structures in the 2D map, where E_{PR} and E_{RA} denote the photon energy for the resonance excitation and the electron energy of the resonant Auger decay, respectively. T_{neu} and T_{ion} denote term values in Si 1s photoexcited states and in resonant Auger final states and effective quantum numbers (n^*) and quantum defects (δ) have been estimated for those states. The quantum number for the Auger final state for V_2 shake-up was estimated to be 5. This value increased from $n = 4$ for the photoexcited state, which is expected for the Si 1s photoexcited state on the assumption of the Rydberg orbital. A single peak was identified for a photoexcited state in the TIY, but two states have been found in the Auger final states: valence type (V_2) and Rydberg type (V_2 shake-up). The estimated intensity ratio was about 1:0.5 for V_2:V_2 shake-up. This finding means that a coupled photoexcited state has disentangled into the two kinetic energies of resonant Auger electrons: two spectator electrons are demonstrated to be involved in these resonant Auger processes. This implies that the single peak in the TIY comes from states composed of some different orbitals, at least two orbitals. The electron kinetic energy spectrum exhibits a projection of the two states when the resonant Auger electrons are measured.

Table I shows that the values of quantum number for the island R at the photon energy of about 1850 eV are 4 and 5 for the photoexcited state and Auger final state, respectively. In the hydrogenic model, the Rydberg orbital (quantum number n) in the singly charged core mainly turns into that of n' for the doubly charged core by the equation, $n' = n[(Z_c + 1)/Z_c]^{1/2}$, where Z_c denotes a core charge [9]. This model supports the change in the quantum number from 4 to 5 in this resonant Auger process. The island of R shake-up is yielded at the same photon energy as that of R. The quantum number for this R shake-up is calculated to be 6 (see Table I). The intensity ratio in the Auger decay is found to be about 1:0.8 for the islands of R:R shake-up. This ratio implies that the shake process significantly affects this Rydberg electron; the shake process is represented by the following:

$$M^*(\mathrm{Si}\ 1s^{-1}nl) \rightarrow M^+(\mathrm{Si}\ 2p^{-2} : {}^1D_2n'l'), \tag{3}$$

One can see that the island R shake-down has a considerable intensity at the electron kinetic energy of about 1606 eV. If the spectator electron exists in a Rydberg orbital, the quantum number of the Auger final state is estimated to be 4 for this island. This estimation is not consistent with the above-mentioned hydrogenic model because the same quantum number was obtained here for both the photoexcited state and the Auger final state. Therefore, the excited orbital is presumably a valence molecular orbital. The term value was calculated to be 12.9 eV, which is close to that for the V_2 island, 13.6 eV. In consideration of the present energy resolution, the resonant Auger final state for the R shake-down may be the same as that for the V_2 island. The scheme for this decay is given as follows:

$$M^*(\mathrm{Si}\ 1s^{-1}nl) \rightarrow M^+(\mathrm{Si}\ 2p^{-2} : {}^1D_2v^*). \tag{4}$$

The intensity ratio for the island R to that for the R shake-down is obtained to be 1: 0.5. There are several possible reasons of this shake effect. One is that a Rydberg electron turns into a valence electron during the change in the core hole from Si 1 s^{-1}, single charge, into Si $2p^{-2}$, double charge. A more probable explanation is as follows. The photoexcited state originates from coupled excitation of several orbitals, Rydberg type and molecular valence type. The coupled state decomposes into resonant Auger final states including an excited electron in two types of orbital. This Auger decay disentangles the coupled state into distinguishable states containing photoexcited orbitals with original characteristics. In other words the resonant Auger transition makes a projection of the coupled orbitals into several electron kinetic energies which give at least two values, in addition to the R shake-up island.

Some tiny structures below the kinetic energy of 1593 eV in Fig. 2 resemble those for the NA long island, the islands of R, R shake-up and V_2 shake-up. These structures probably come from resonant Auger decays of the Si $2p^{-2}$: $^1S_0$ core hole in the final states. The spectator electron in this instance seems to behave similarly to that of the $^1D_2$ core hole. A structure in the $^1S_0$ series corresponding to the island V_2 may be overlapped with the island V_2 shake-up for the $^1D_2$ core hole.

Resonant Si $KL_{23}L_{23}$ Auger electron spectra for the perpendicular photon polarization were measured and revealed the same characteristics as those for the parallel polarization. The electron kinetic energies and term values obtained are in agreement with those listed in Table I. Resonant Auger transitions into states with another core hole, 2 $s^{-1}2p^{-1}$: ^1P, were also measured by the same procedure. Although intensities for island structures are low, the 2D map for the final states of the 2 $s^{-1}2p^{-1}$: ^1P series exhibits clear islands corresponding to those of V_2, V_2 shake-up, R and R shake-up for the $^1D_2$ core hole. A faint island for R shake-down is seen marginally. The energy for NA decay into ^1P was observed at

TABLE I. Main structures in the two-dimensional map of electron spectra (in units of eV). See the text for an explanation of several labels such as R, V_1, T_{neu}, and n^*. Values in parentheses denote those estimated on the assumption that relevant orbitals are of Rydberg type.

Label	E_{PR}	T_{neu}	n^*	n	δ	E_{RA}	T_{ion}	n^*	n	δ
$KL_{23}L_{23}$ resonant Auger										
V_1	1846.1	6.2				1604.8	15.7			
V_2	1848.5	3.8				1605.1	13.6			
V_2 shake-up	1848.9	3.4	(2.0	4	2.0)	1598.8	6.9	2.8	5	2.2
R	1849.9	2.4	2.4	4	1.6	1599.7	6.8	2.8	5	2.2
R shake-up	1850.3	2.0	2.6	4	1.4	1597.1	3.8	3.8	6	2.2
R shake-down	1850.2	2.1	2.5	4	1.5	1606.1	12.9	(2.1	4	2.0)
KL_1L_{23} resonant Auger										
V_2	1848.3	4.0				1547.2	13.6			
V_2 shake-up	1848.7	3.6	(1.9	4	2.1)	1541.1	7.1	2.8	5	2.2
R	1849.9	2.4	2.4	4	1.6	1541.2	6.0	3.0	5	2.0
R shake-up	1850.0	1.8	2.8	4	1.3	1539.5	3.7	3.8	6	2.2
R shake-down	1849.9	2.4	2.4	4	1.6	1547.7	12.5	(2.1	4	1.9)

1537.7 eV, which agrees with the value in the literature [11]. The term values estimated for these islands are listed at the lower part in Table I. These energies are in agreement with those for the final states of the $^1D_2$ series.

IV. CONCLUSION

Spectator resonant Auger electron spectra of Si 1s photoexcitation of SiF_4 have been measured as a function of the photon energy near the Si 1s ionization threshold. The second peak of photoabsorption at 1848.5 eV induces shake-up transition from the valence orbital into a Rydberg orbital, whereas the third peak at 1849.9 eV generates shake-up and shake-down transitions from a Rydberg orbital into a higher Rydberg orbital and into a valence molecular orbital, respectively. These two kinds of shake processes probably originate from mixing effects of excited orbitals which are populated by photoabsorption. These excited orbitals are disentangled into original components in the resonant Auger decays. This disentanglement provides the projection of the excited orbitals into electron kinetic energies. This conjecture is consistent with the calculation of the photoexcitation spectrum within the framework of DFT.

ACKNOWLEDGMENTS

The authors wish to express sincere thanks to the members of the research team for soft X-ray photochemistry for their fruitful comments, and to the staff of SPring-8 facility for their assistance during the course of the experiments. I.H.S. expresses appreciation for support during this study from Professor Kenji Ito of Photon Factory. This study was carried out with the approval of the SPring-8 Program Advisory Committee (Proposal No. 2009A1085).

[1] M. Kato, Y. Morishita, M. Oura, H. Yamaoka, Y. Tamenori, K. Okada, T. Matsudo, T. Gejo, I. H. Suzuki, and N. Saito, J. Electron Spectrosc. Relat. Phenom. **160**, 39 (2007).

[2] S. Bodeur, P. Millie, and I. Nenner, Phys. Rev. A **41**, 252 (1990).

[3] C. Kolczewski *et al.*, J. Chem. Phys. **115**, 6426 (2001).

[4] O. Takahashi, I. H. Suzuki, Y. Kono, A. Ikeda, T. Ouchi, K. Ueda, I. Higuchi, Y. Tamenori, and S. Nagaoka, J. Phys. Conf. Ser. **235**, 012018 (2010).

[5] S. Aksela, K. H. Tan, H. Aksela, and G. M. Bancroft, Phys. Rev. A **33**, 258 (1986).

[6] G. G. B. de Souza, P. Morin, and I. Nenner, J. Chem. Phys. **90**, 7071 (1989).

[7] T. A. Ferrett, M. N. Piancastelli, D. W. Lindle, P. A. Heimann, and D. A. Shirley, Phys. Rev. A **38**, 701 (1988).

[8] C. Miron, R. Guillemin, N. Leclercq, P. Morin, and M. Simon, J. Electron Spectrosc. Relat. Phenom. **93**, 95 (1998).

[9] G. B. Armen, J. Phys. B **29**, 677 (1996).

[10] K. Okada, M. Kosugi, A. Fujii, S. Nagaoka, T. Ibuki, S. Samori, Y. Tamenori, H. Ohashi, I. H. Suzuki, and K. Ohno, J. Phys. B **38**, 421 (2005).

[11] P. Kelfve, B. Blomster, H. Siegbahn, K. Siegbahn, E. Sanhueza, and O. Goscinski, Phys. Scr. **21**, 75 (1980).

[12] I. H. Suzuki, A. Nitta, H. Fukuzawa, K. Ueda, O. Takahashi, Y. Tamenori, and S. Nagaoka, J. Chem. Phys. **131**, 164309 (2009).

[13] H. Ohashi, E. Ishiguro, Y. Tamenori, H. Kishimoto, M. Tanaka, M. Irie, T. Tanaka, and T. Ishikawa, Nucl. Instrum. Methods A **467**, 529 (2001).

[14] V. Schmidt, *Electron Spectrometry of Atoms using Synchrotron Radiation* (Cambridge University Press, Cambridge, 1997), Chapter 6.

[15] K. Siegbahn *et al.*, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969), pp. 156–163.