Dependence of Chemical Shift Difference on Core-Level

Umpei Nagashima*[1] and Shin-ichi Nagaoka[2]

[1]Research Institute for Computational Sciences, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba 305-8568

[2]Department of Chemistry, Faculty of Science and Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577

Received April 24, 2009
E-mail: u.nagashima@aist.go.jp

A reason for the greater chemical shift difference observed in a deep core level than a shallow level is presented.

In a previous paper, Nagaoka et al. reported high-resolution core-photoelectron spectra of $F_3SiCH_2CH_2Si(CH_3)_3$ (FSMSE), which has two Si atoms: one is bonded to three fluorine atoms (here denoted Si[F]) while the other is bonded to three methyl groups (Si[Me]).[1,2] Since core-level ionization energies depend on the local chemical environment of the atom inside the molecule, the Si[F] and Si[Me] atoms show different chemical shifts. As a result, in the Si core-photoelectron spectrum of FSMSE one can resolve two peaks whose positions reflect the chemical shifts due to the different chemical environments. It was shown that the chemical shift difference between the Si[Me] and Si[F] sites (ΔE) in the Si:1s core-photoelectron spectrum is 3.9 eV, which is larger than ΔE in the Si:2p and 2s core-photoelectron spectrum (3.4 and 3.1 eV, respectively).[1,2] Thus, ΔE for the K shell (ΔE_K) is larger than that for the L shell (ΔE_L), and ΔE's for the 1s, 2p, and 2s ionizations decrease in that order (1s > 2p > 2s), which is different from the order of the binding energy (1s > 2s > 2p).

A large value for a chemical shift difference in a deeper core-level compared to the corresponding value for a shallower level was also observed in various systems.[3–8] In a recent paper, Lundwall et al. theoretically considered the shell-dependent core-level chemical shifts observed in free xenon clusters, but they could not find a conclusive explanation.[8] Like this, solid reasons for the dependence of the chemical shift difference on the core-level remain unknown. Accordingly, an intuitive and qualitative model for understanding the accumulated experimental data are highly desirable. Although we previously explained the existence of the chemical shift on the basis of the description in Ref. 9,[10,11] the explanation cannot successfully give the shell-dependent chemical shift. In this paper, we will propose a more detailed explanation than the one given in Refs. 10 and 11.

A core electron of a Si atom in FSMSE experiences a Coulombic repulsion due to the presence of all other electrons. If the core electron is at a distance r from the Si nucleus, it experiences a repulsion that can be represented by a negative point charge located at the nucleus and equal in magnitude to the total charge of the electrons within a sphere of radius r.[12] This point negative charge reduces the full positive charge of the Si nucleus from $14e$ to Z^*e, and the core electron experiences the shielded nuclear charge. Here e and Z^*e denote elementary charge and effective nuclear charge, respectively. According to Slater's rule[13] the Z^* values for the K and L shells of Si are 13.70 and 9.85, respectively. In a simple physical picture, applicable to many electron atoms,[14] the core binding energy (E) is given by

$$E = RZ^{*2}/n^2 \quad (1)$$

where n denotes the principal quantum number of the core–shell and R is a constant ($R = 313.6\,\mathrm{kcal\,mol^{-1}}$, $1\,\mathrm{kcal} = 4.184\,\mathrm{kJ}$).

Some of the valence electrons of FSMSE penetrate even through the core shells to regions near the Si nucleus, although the probability is not large. Since the electron-donating property of a methyl group is larger than that of a fluorine atom, the penetration at the Si[Me] atom is stronger than that at the Si[F] atom. As a result, the Si[Me] nucleus is shielded more than the Si[F] nucleus, Z^* for Si[Me] (Z^*_{Me}) is less than that for Si[F] (Z^*_F), and therefore E for Si[Me] is less than that for Si[F] (eq 1). Then, ΔE is given by

$$\Delta E = R({Z^*_F}^2 - {Z^*_{Me}}^2)/n^2 \quad (2)$$

When we let Z^*_X (X = F or Me) for the K (L) shell be $Z^*_{K,X}$ ($Z^*_{L,X}$),

$$\begin{aligned}\Delta E_K/\Delta E_L &= 4({Z^*_{K,F}}^2 - {Z^*_{K,Me}}^2)/({Z^*_{L,F}}^2 - {Z^*_{L,Me}}^2)\\ &= 4(Z^*_{K,F} + Z^*_{K,Me})(Z^*_{K,F} - Z^*_{K,Me})\\ &\quad \div \{(Z^*_{L,F} + Z^*_{L,Me})(Z^*_{L,F} - Z^*_{L,Me})\} \quad (3)\end{aligned}$$

Since $Z^*_{K,F} + Z^*_{K,Me} \approx 27.40$ and $Z^*_{L,F} + Z^*_{L,Me} \approx 19.70$,[13]

$$\Delta E_K/\Delta E_L \approx 5.563(Z^*_{K,F} - Z^*_{K,Me})/(Z^*_{L,F} - Z^*_{L,Me}) \quad (4)$$

The value of $(Z^*_{K,F} - Z^*_{K,Me})/(Z^*_{L,F} - Z^*_{L,Me})$ should not be extremely far from unity (that is, it should be $>1/5.563$), because in Slater's rule[13] the increase in Z^* for the K shell is equal to that for the L shell when the nuclear charge increases from $14e$ to $15e$ or from $13e$ to $14e$ (large perturbation): the change in Z^* by the substituent effect (small perturbation) for the K shell ($Z^*_{K,F} - Z^*_{K,Me}$) would not be extremely different from that for the L shell ($Z^*_{L,F} - Z^*_{L,Me}$), either. Accordingly, judging from eq 4, ΔE_K should be larger than ΔE_L. Although this explanation is based on a rough approximation, it is consistent with the experimental results.[1–8]

Next, we quantitatively examine the explanation given above. The ab initio molecular-orbital calculations for FSMSE were performed by using the Gaussian 03 program,[15] and the core binding energies were estimated on the basis of Koopmans' theorem. At the HF/6-311++G**//HF/6-311++G** level ΔE_K (3.43 eV) was larger than ΔE_L (3.21 eV for 2s and 3.24 eV for 2p), and the result is consistent with the model given above. The $\Delta E_K/\Delta E_L$ value for the s orbital (1.07) is similar to the corresponding experimental value (1.3).[1,2]

Published on the web October 8, 2009; doi:10.1246/bcsj.82.1248

We also tried to evaluate the dependence of the chemical shift difference on the core-level for typical electron-donating and -accepting substituents; that is, to evaluate the value corresponding to $\Delta E_K/\Delta E_L$ for typical electron-donating and -accepting substituents. The Mulliken atomic charges of Si[Me] and Si[F] in FSMSE were calculated to be 0.13 and 1.37 respectively at the HF/6-311++G**//HF/6-311++G** level. Accordingly, the typical dependence mentioned above may be evaluated by using the chemical shift difference between Si and Si^+ (ΔE°) in which the atomic charges are 0 and 1, respectively. Here as a model of atoms in a molecule, we assumed that Si and Si^+ have quintet and quartet states, respectively. Let ΔE° for the K and L shells be $\Delta E_K{}^\circ$ and $\Delta E_L{}^\circ$, respectively. In this extreme case again $\Delta E_K{}^\circ$ was slightly larger than $\Delta E_L{}^\circ$ and $\Delta E_K{}^\circ/\Delta E_L{}^\circ$ for the s orbital was calculated to be 1.02 at the HF/6-311G** level, which is equivalent to HF/6-311++G** in atoms. Accordingly, the chemical shift difference for the K shell would be generally larger than that for the L shell.

In both of the above-mentioned experimental and computational results of FSMSE, ΔE's for the 1s, 2p, and 2s ionizations decrease in that order (1s > 2p > 2s), which is different from the order of the binding energy (1s > 2s > 2p). The reason for this may be that the average distance from the Si nucleus to the 2p electron is less than that to the 2s electron and closer to that to the 1s electron (1s < 2p < 2s).[14,16] Thus the substituent effect on the nuclear shielding by the Si:1s electrons is more similar to that by the Si:2p electrons than to that by the Si:2s electrons; that is, ${Z^*}_F^2 - {Z^*}_{Me}^2$ in eq 2 for the 1s orbital is more similar to that by the 2p orbital than to that by the 2s orbital. Note that an inner orbital such as an s orbital in an electron shell ($n \geq 2$) is often expanded more than an outer orbital such as a p or d orbital in the same electron shell if the nephelauxetic effect is absent.[17]

It is necessary to critically examine the above-mentioned computational results. Although quantitativity of Koopmans' theorem and the Mulliken atomic charge here employed is doubtful, these concepts are widely used and helpful in qualitative discussion. However, quantitative estimation of ionization energies and ΔE may be difficult. For example, the ΔE-difference between 2s and 2p was calculated to be 0.03 eV, which was much less than the experimental value (0.3 eV), because the calculations did not include the orbital reorganization induced by core ionization.

In this communication we have explained the reason why a chemical shift difference in a deeper core-level is larger than that in a shallower one. Although our explanation is qualitative, it is intuitive and consistent with the experimental results.

We express our sincere thanks to Dr. Isao H. Suzuki of Institute of Materials Structure Science for his valuable discussion. This work was supported by a Grant-in-Aid for Scientific Research (C) (No. 19550020) from Japan Society for the Promotion of Science (JSPS).

References

1 S. Nagaoka, M. Takemoto, G. Prümper, H. Fukuzawa, Y. Tamenori, I. H. Suzuki, K. Ueda, *J. Chem. Phys.* **2008**, *129*, 204309.

2 I. H. Suzuki, A. Nitta, A. Shimizu, Y. Tamenori, H. Fukuzawa, K. Ueda, S. Nagaoka, *J. Electron Spectrosc. Relat. Phenom.* **2009**, *173*, 18.

3 O. Keski-Rahkonen, M. O. Krause, *J. Electron Spectrosc. Relat. Phenom.* **1976**, *9*, 371.

4 R. N. Sodhi, R. G. Cavell, *J. Electron Spectrosc. Relat. Phenom.* **1983**, *32*, 283.

5 R. N. S. Sodhi, R. G. Cavell, *J. Electron Spectrosc. Relat. Phenom.* **1986**, *41*, 1.

6 S. Bodeur, I. Nenner, P. Millie, *Phys. Rev. A* **1986**, *34*, 2986.

7 Th. Eickhoff, V. Medicherla, W. Drube, *J. Electron Spectrosc. Relat. Phenom.* **2004**, *137–140*, 85.

8 M. Lundwall, R. F. Fink, M. Tchaplyguine, A. Lindblad, G. Öhrwall, H. Bergersen, S. Peredkov, T. Rander, S. Svensson, O. Björneholm, *J. Phys. B: At. Mol. Phys.* **2006**, *39*, 5225.

9 K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, Y. Baer, *ESCA Applied to Free Molecules*, North-Holland, Amsterdam, **1969**, pp. 104–109.

10 S. Nagaoka, J. Ohshita, M. Ishikawa, K. Takano, U. Nagashima, T. Takeuchi, I. Koyano, *J. Chem. Phys.* **1995**, *102*, 6078.

11 S. Nagaoka, U. Nagashima, J. Ohshita, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 537.

12 P. Atkins, J. de Paula, *Atkins' Physical Chemistry*, 7th ed., Oxford University Press, Oxford, **2002**, p. 386.

13 J. A. Pople, D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, **1970**, pp. 22–30.

14 G. C. Pimentel, R. D. Spratley, *Chemical Bonding Clarified through Quantum Mechanics*, Holden-Day, San Francisco, **1969**, Chaps. 1 and 2.

15 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision E.01*, Gaussian, Inc., Wallingford CT, **2004**.

16 C. F. Fischer, *The Hartree–Fock Method for Atoms—A Numerical Approach*, Wiley, New York, **1977**, p. 32.

17 N. Azuma, Y. Imori, H. Yoshida, K. Tajima, Y. Li, J. Yamauchi, *Inorg. Chim. Acta* **1997**, *266*, 29.