Relativistic Effect on ^{77}Se NMR Chemical Shifts of Various Selenium Species in the Framework of Zeroth-Order Regular Approximation

S. Hayashi, Y. Katsura, and W. Nakanishi*

Department of Material Science and Chemistry, Faculty of Systems Engineering, Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan; E-mail: hayashi3@sys.wakayama-u.ac.jp

The relativistic effect on absolute magnetic shielding tensors ($\sigma(N)$) became to evaluate successfully under the zeroth-order regular approximation (ZORA) level [1]. Eq 1 explains the outline briefly [2], where $V(\boldsymbol{r})$ is the effective Kohn-Sham potential in external magnetic field $\boldsymbol{B}$ within the DFT theory, $\boldsymbol{\sigma}$ are the Pauli matrices, and c is the speed of light. $\boldsymbol{\pi}$ and $K(\boldsymbol{r})$ are given by eq 2. The first two terms in eq 1 form the basis of the scalar relativistic approximation and the third term represents spin-orbit coupling. As shown in eq 3, $\sigma^{t}(N)$ are expressed as the sum of $\sigma^{d}(N)$, $\sigma^{p}(N)$, and $\sigma^{so}(N)$ (the contributions from the spin-orbit interaction terms), if evaluated at the spin-orbit ZORA relativistic level. $\sigma^{d}(N) + \sigma^{p}(N)$ (= $\sigma^{d+p}(N)$) in eq 3 correspond to the first two terms in eq 1, whereas $\sigma^{so}(N)$ originate inherently as the spin-orbit effect.

$$H_{ZORA} = V(\boldsymbol{r}) + \boldsymbol{\pi}(K(\boldsymbol{r})/2)\boldsymbol{\pi} + (K^2(\boldsymbol{r})/4c^2)\boldsymbol{\sigma}\bullet[\nabla V(\boldsymbol{r})\times\boldsymbol{p}] - K(\boldsymbol{r})/c)\boldsymbol{\sigma}\bullet\boldsymbol{p} \quad (1)$$

$$\boldsymbol{\pi} = \boldsymbol{p} + (1/c)\boldsymbol{A}(\boldsymbol{r}),\ \ \boldsymbol{B} = \nabla\times\boldsymbol{A}(\boldsymbol{r});\ \ K(\boldsymbol{r}) = \{1 - (V(\boldsymbol{r})/2c^2)\}^{-1} \quad (2)$$

$$\sigma^{t}(N) = \sigma^{d}(N) + \sigma^{p}(N) + \sigma^{so}(N) = \sigma^{d+p}(N) + \sigma^{so}(N) \quad (3)$$

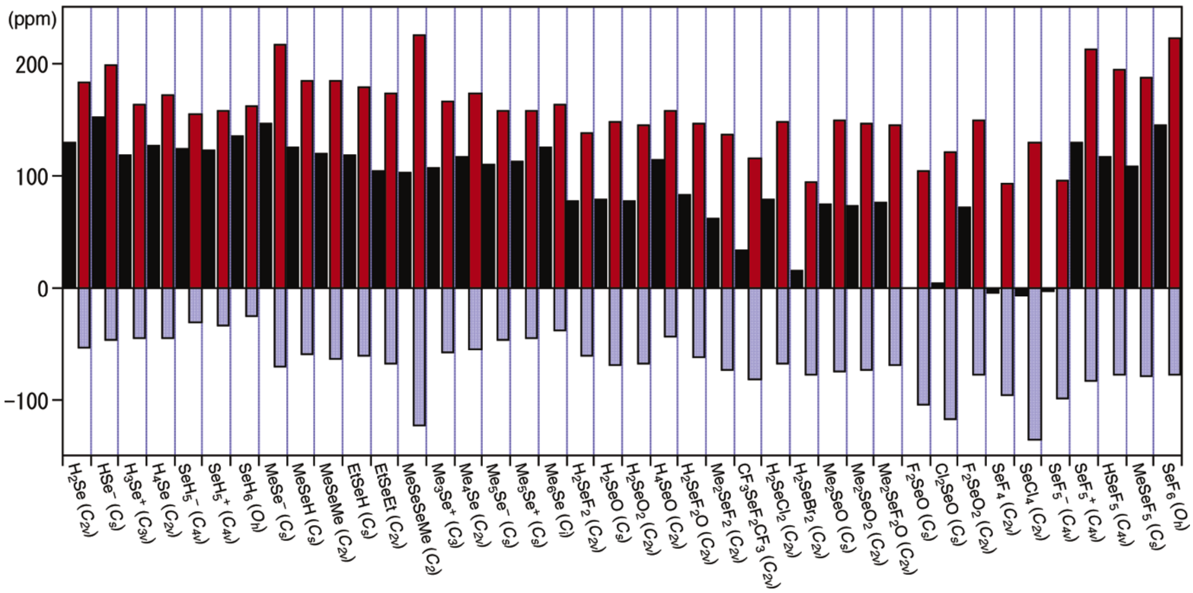

Fig. 1 Relativistic effect on σ(Se) for various selenium compounds: black, blue, and red stand for the total term ($\Delta\sigma^{t}(\mathrm{Se})_{\mathrm{Rlt\text{-}so}} = \Delta\sigma^{d+p}(\mathrm{Se})_{\mathrm{Rlt\text{-}so}} + \sigma^{so}(\mathrm{Se})_{\mathrm{Rlt\text{-}so}}$), the scalar term ($\Delta\sigma^{d+p}(\mathrm{Se})_{\mathrm{Rlt\text{-}so}}$), and the spin-orbit term ($\sigma^{so}(\mathrm{Se})_{\mathrm{Rlt\text{-}so}}$), respectively.

The relativistic effect on σ(Se) are explicitly evaluated for various selenium species with the DFT(BLYP)-GIAO method. Calculations are performed under relativistic and nonrelativistic conditions with the Slater-type basis sets in ADF 2010 in the framework of ZORA, employing the optimized structures under nonrelativistic conditions at B3LYP of Gaussian 03. Figure 1 shows the results. Details will be discussed in the presentation.

[1] *Calculation of NMR and EPR Parameters; Theory and Applications* (Eds.: M. Kaupp, M. Bühl, V.G. Malkin), Wiley-VCH, Weinheim, 2004.

[2] S.K. Wolff, T. Ziegler, *J. Chem. Phys.* **1998**, *109*, 895–905; S.K. Wolff, T. Ziegler, E. van Lenthe, E.J. Baerends, *J. Chem. Phys.* **1999**, *110*, 7689–7698; J.R. Yates, C.J. Pickard, M.C. Payne, F. Mauri, *J. Chem. Phys.* **2003**, *118*, 5746–5753.