

Supporting Information for

Scandium and Yttrium Environments in Aluminosilicate Glasses Unveiled by $^{45}\text{Sc}/^{89}\text{Y}$ NMR Spectroscopy and DFT Calculations: What Structural Factors Dictate the Chemical Shifts?

Aleksander Jaworski^a, Thibault Charpentier^b, Baltzar Stevansson^a, and Mattias Edén^{a,*}

^aPhysical Chemistry Division, Department of Materials and Environmental Chemistry,
Stockholm University, SE-106 91 Stockholm, Sweden

^bNIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette cedex, France

*Corresponding author. E-mail address: *mattias.eden@mmk.su.se*

Contents

1. **Section S1.** Implementation of the DFT+ U Procedure.
2. **Figure S1.** ^{17}O NMR References.
3. **Figure S2.** ^{17}O NMR Shifts for Sc_2O_3 and YAlO_3 .
4. **Figure S3.** ^{45}Sc NMR Shifts for Sc_2O_3 from “Direct” and U -Corrected Calculations.
5. **References**

S1. Implementation of the DFT+ U Procedure

For several elements, such as Ca, Sc, and La, electronic structure calculations at the PBE-DFT level of theory are prone to overestimating the hybridization between the $2p$ O orbital and the unoccupied $3d^0$ and $4f^0$ cation-localized orbitals. This results in an emphasized covalent bonding character, thereby deteriorating the accuracy of the NMR parameter predictions.^{S1-S4} To remedy this problem, here we employ the “DFT+ U ” approach,^{S1,S2} which involves an artificial shift (U) of the $3d^0$ (Sc) and $4f^0$ (Y) states towards higher energy to reduce the bond covalency and better reproduce the experimentally determined NMR chemical shifts.

To locate suitable values of U for ^{45}Sc and ^{89}Y , ^{17}O isotropic chemicals shifts of some reference structures were exploited, whose experimental values are available and for which the PBE-DFT/GIPAW framework provides accurate predictions: Na_2MoO_4 , SiO_2 (quartz), $\alpha\text{-Al}_2\text{O}_3$ and NaAlO_2 (see **Figure S1**). Linear regression of the data using the equation

$$\delta_{\text{iso}}^j = -\alpha(\sigma_{\text{iso}}^{\text{S},j} - \sigma_{\text{iso}}^{\text{S},\text{ref}}) \quad (\text{S1})$$

provided a slope very close to unity ($\alpha = 0.99$), and $\sigma_{\text{iso}}^{\text{S},\text{ref}} = 256.4$ ppm. However, the ^{17}O chemical shifts of Sc_2O_3 and YAlO_3 deviate significantly to the regression results. Following the procedures discussed in refs. S1 and S2, the value of U was determined such that the predicted $\sigma_{\text{iso}}^{\text{S},j}$ result matches the regression, yielding the optimal U energy shifts of 5.0 eV ($3d^0$) and 2.8 eV ($4f^0$) for Sc and Y, respectively, as illustrated in **Figure S2**. The results of **Figure S3** reveal significantly improved ^{45}Sc chemical shift predictions when the DFT+ U approach was applied to Sc_2O_3 [eq S1].

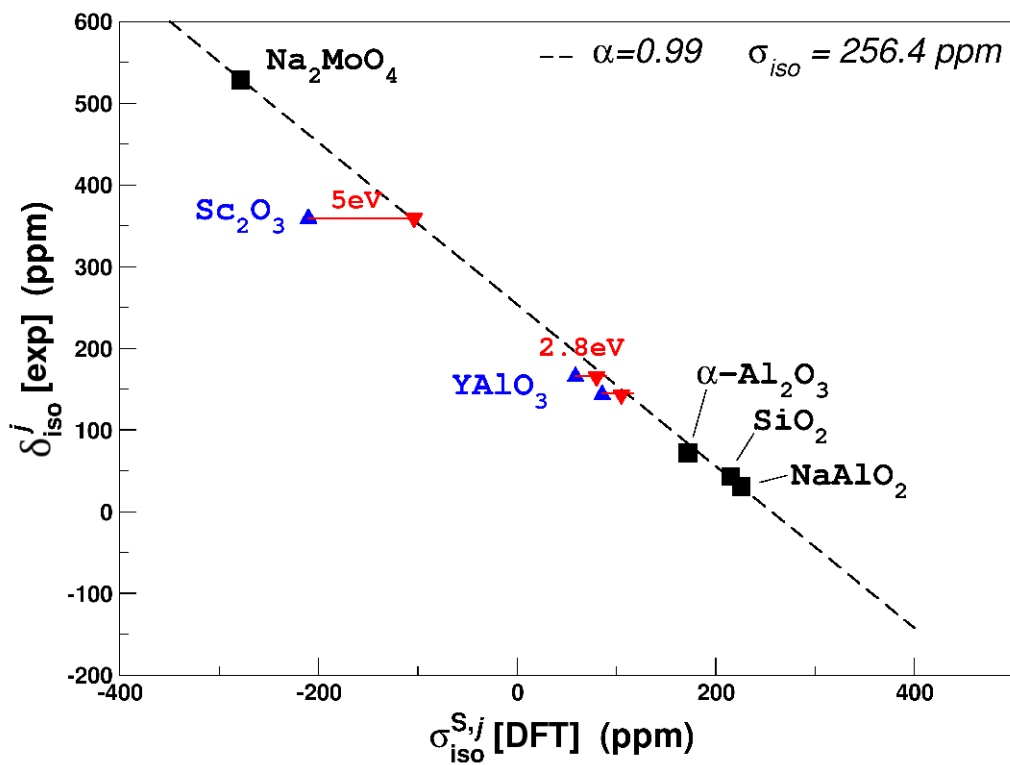


Figure S1. Experimental ^{17}O NMR isotropic chemical shifts plotted against their corresponding PBE-DFT/GIPAW calculated $\sigma_{\text{iso}}^{S,j}$ -values (black squares) for the as-indicated reference structures, and the resulting regression line. Results for ^{17}O sites of Sc_2O_3 and YAlO_3 from the uncorrected PBE-DFT/GIPAW calculations are provided as blue triangles, whereas red triangles show the results from employing U -corrections of 5.0 eV ($3d^0$) and 2.8 eV ($4f^0$) for Sc and Y, respectively.

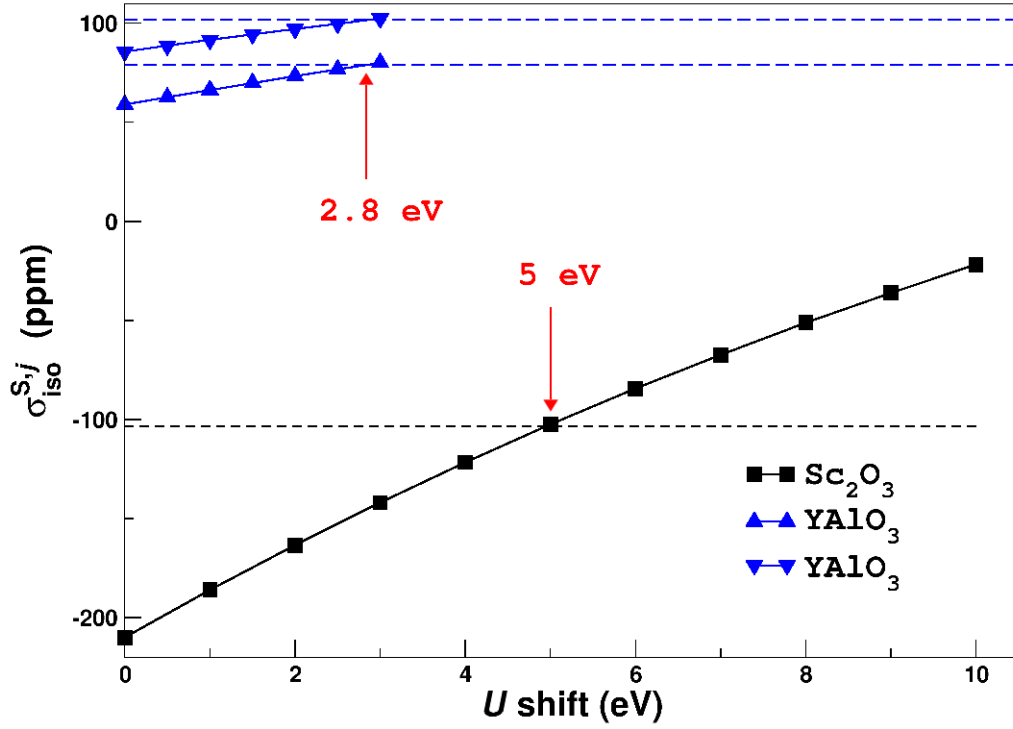


Figure S2. Dependence of the calculated ^{17}O $\sigma_{\text{iso}}^{S,j}$ -values on the U energy shift of $3d^0$ and $4f^0$ states for Sc and Y, respectively, as presented for Sc_2O_3 (black squares) and YAlO_3 (blue triangles). Each point represents the result of an individual DFT+ U calculation upon a stepwise U -value adjustment. Dashed lines correspond to the case of coinciding experimental and DFT+ U /GIPAW-derived ^{17}O $\sigma_{\text{iso}}^{S,j}$ -values, establishing our computational setup for evaluation of the ^{45}Sc and ^{89}Y chemical shifts in the glass models.

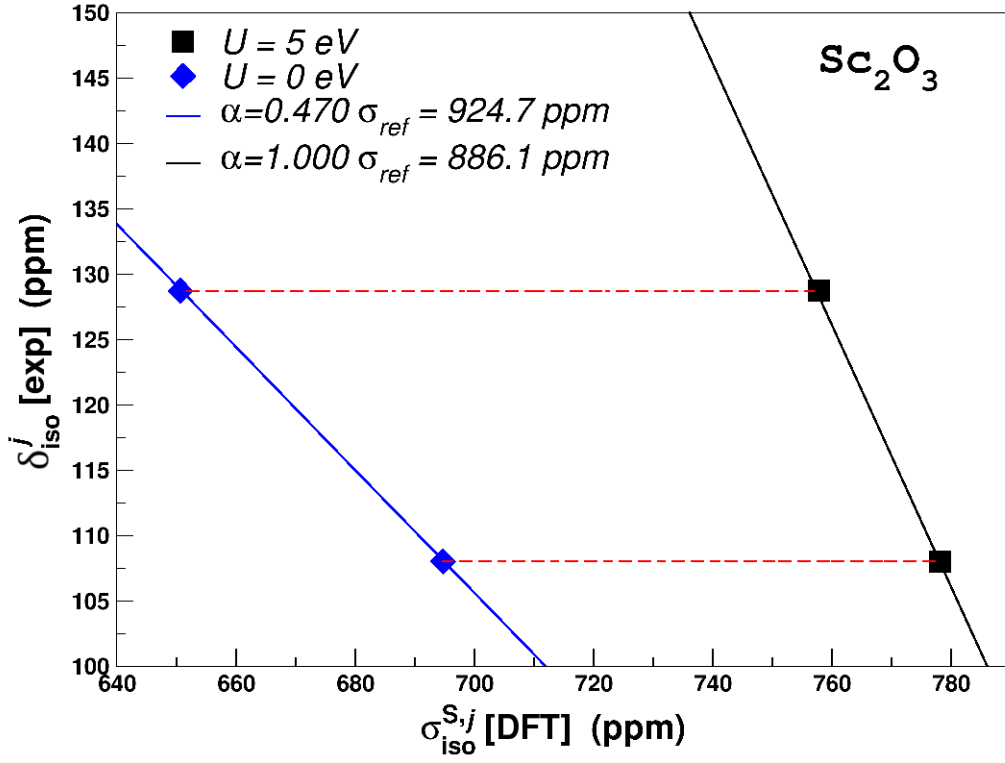


Figure S3. Experimental NMR-derived ^{45}Sc isotropic chemical shifts and the corresponding $\sigma_{\text{iso}}^{S,j}$ -values calculated at the PBE-DFT/GIPAW level of theory for the two inequivalent ^{45}Sc sites of Sc_2O_3 . Blue and black squares represent the uncorrected and U -corrected results, respectively. The unity slope associated with the experimental NMR (δ_{iso}^j) and GIPAW-derived U -corrected ($\sigma_{\text{iso}}^{S,j}$) ^{45}Sc results validates our employed $3d^0$ energy-shift value of 5.0 eV for Sc.

References

- (S1) Profeta, M.; Benoit, M.; Mauri, F.; Pickard, C. First-Principles Calculation of the ^{17}O NMR Parameters in Ca Oxide and Ca Aluminosilicates: The Partially Covalent Nature of the Ca–O Bond, a Challenge for Density Functional Theory. *J. Am. Chem. Soc.* **2004**, *126*, 12628–12635.
- (S2) Sadoc, A.; Body, M.; Legein, C.; Biswal, M.; Fayon, F.; Rocquefelte, X.; Boucher, F. NMR Parameters in Alkali, Alkaline Earth and Rare Earth Fluorides from First Principle Calculations. *Phys. Chem. Chem. Phys.* **2011**, *13*, 18539–18550.
- (S3) Gervais, C.; Laurencin, D.; Wong, A.; Pourpoint, F.; Labram, J.; Woodward, B.; Howes, A.; Pike, K. J.; Dupree, R.; Mauri, F.; Bonhomme, C.; Smith, M. E. New Perspectives on Calcium Environments in Inorganic Materials Containing Calcium-Oxygen Bonds: A Combined Computational-Experimental ^{43}Ca NMR Approach. *Chem. Phys. Lett.* **2008**, *464*, 42–48.
- (S4) Benoit, M.; Profeta, M.; Mauri, F.; Pickard, C.; Tuckerman, M. First-Principles Calculation of the ^{17}O NMR Parameters of a Calcium Aluminosilicate Glass. *J. Phys. Chem. B* **2005**, *109*, 6052–6060.