Supporting information

Theoretical and Experimental Insights into Applicability of Solid-State $^{93}$Nb NMR in Catalysis

Evgeniy PAPULOVSKIY$^{1,2}$, Alexandre A. SHUBÌN$^{1,2}$, Victor V. TERSKÌKH$^{3}$, Christopher PICKARD$^{4,*}$ and Olga B. LAPINA$^{1,2,*}$

$^1$ Boreskov Institute of Catalysis, 630090 Novosibirsk, Russia
$^2$ Novosibirsk State University, 630090 Novosibirsk, Russia
$^3$ Emerging Technologies Division, National Research Council Canada, Ottawa, Ontario, Canada K1A 0R6
$^4$ University College London, London, United Kingdom WC1E 6BT

* corresponding authors:

Christopher Pickard, University College London, London, United Kingdom WC1E 6BT, c.pickard@ucl.ac.uk
Olga B. LAPINA, Boreskov Institute of Catalysis, Novosibirsk, Russia 630090, phone: +73833269505, fax: +7 3833 30 80 56, olga@catalysis.ru
Figure S1. $^{93}$Nb NMR spectra of a stationary powdered sample of $\text{YNbO}_4$ acquired at 9.4 T (left) and at 21.1 T (right). (1) Experimental spectra, (2) Simulated spectra with NMR parameters determined in [1] from the experimental spectra, $\delta_{\text{iso}} = -845$ ppm, $\delta_{\delta} = -200$ ppm, $\eta_{\delta} = 0.480$, $C_Q = 82.00$ MHz, $\eta_Q = 0.38$, $\alpha, \beta, \gamma = 15, 16, 80$, (3) Simulated spectra with NMR parameters obtained via GIPAW calculations, $\delta_{\text{iso}} = -901$ ppm, $\delta_{\delta} = -191$ ppm, $\eta_{\delta} = 0.515$, $C_Q = 76.4$ MHz, $\eta_Q = 0.41$, $\alpha, \beta, \gamma = 180, 21, 90$. 

Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics
This journal is © The Owner Societies 2013
Figure S2. $^{93}$Nb NMR spectra of a stationary powdered sample of LaNbO$_4$ acquired at 9.4 T (left) and at 21.1 T (right). (1) Experimental spectra. (2) Simulated spectra with NMR parameters determined in [2] from the experimental spectra, $\delta_{\text{iso}} = -853$ ppm, $\delta_\delta = -238$ ppm, $\eta_\delta = 0.559$, $\nu_Q = 86.55$ MHz, $\eta_Q = 0.19$, $\alpha, \beta, \gamma = 13, 11, 85$. (3) Simulated spectra with NMR parameters obtained via GIPAW calculations, $\delta_{\text{iso}} = -818$ ppm, $\delta_\delta = -225$ ppm, $\eta_\delta = 0.625$, $\nu_Q = 95.30$ MHz, $\eta_Q = 0.11$, $\alpha, \beta, \gamma = 0.9, 90$. (*) indicates an impurity.
Figure S3. $^{93}$Nb NMR spectra of a stationary powdered sample of Li$_3$NbO$_4$ acquired at 9.4 T. 

(1) Experimental spectrum. (2) Simulated spectrum using experimental NMR parameters determined in [1] from the experimental spectra, $\delta_{\text{iso}} = -946$ ppm, $\delta_\delta = 135$ ppm, $\eta_\delta = 0.3$, $C_Q = 11.5$ MHz, $\eta_Q = 0.1$, $\alpha, \beta, \gamma = 0,0,0$. (3) Simulated spectrum using GIPAW calculated parameters for the optimized structure (see text), $\delta_{\text{iso}} = -893$ ppm, $\delta_\delta = 125$ ppm, $\eta_\delta = 0.0$, $C_Q = -16.1$ MHz, $\eta_Q = 0.0$, $\alpha, \beta, \gamma = 79,0,76$. 
Figure S4. $^{93}$Nb NMR spectra of LiNbO$_3$ (I) ($\text{Li}_{0.938}\text{Nb}_{0.012}\text{NbO}_3$) at 9.4 T acquired under stationary conditions (left) and under 30 kHz MAS (right). (1) Experimental spectra. (2) Simulated spectra based on experimental data, $\delta_{\text{iso}} = -1005$ ppm, $\delta_\delta = 75$ ppm, $\eta_\delta$ = 0.007, $C_Q$ = 21.5 MHz, $\eta_Q$ = 0.0, $\alpha, \beta, \gamma = 126, 0, 85$, Gaussian distribution of $C_Q$ with 3 MHz width. (3) Simulated spectra using NMR parameters obtained by GIPAW for LiNbO$_3$ (I), $\delta_{\text{iso}} = -940$ ppm, $\delta_\delta = 101$ ppm, $\eta_\delta$ = 0.007, $C_Q$ = 19.34 MHz, $\eta_Q$ = 0.0, $\alpha, \beta, \gamma = 126, 0, 85$. 

Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics
This journal is © The Owner Societies 2013
Figure S5. $^{93}$Nb NMR spectra of KNbO$_3$ at 9.4 T acquired under stationary conditions in (A) and under 29 kHz MAS in (B). (1) Experimental spectra. (2) Simulated spectra using NMR parameters determined in this work from the experimental spectra, $\delta_{\text{iso}} = -1007$ ppm, $\delta_{\delta} = -60$ ppm, $\eta_{\delta} = 0.30$, $C_Q = 22.00$ MHz, $\eta_Q = 0.82$, $\alpha,\beta,\gamma = 20,90,90$. (3) Simulated spectra with NMR parameters obtained via GIPAW calculations, $\delta_{\text{iso}} = -935$ ppm, $\delta_{\delta} = -60$ ppm, $\eta_{\delta} = 0.743$, $C_Q = -21.56$ MHz, $\eta_Q = 0.96$, $\alpha,\beta,\gamma = 114,90,90$. 
Figure S6. $^{93}$Nb NMR spectra of a stationary powdered sample of CaNb$_2$O$_6$ acquired at 9.4 T. (1) Experimental spectrum. (2) Simulated spectrum with NMR parameters determined in [2] based on the experimental spectra, $\delta_{\text{iso}} = -975$ ppm, $\delta_\delta = -291$ ppm, $\eta_\delta = 0.619$, $C_Q = 50.40$ MHz, $\eta_Q = 0.787$, $\alpha, \beta, \gamma = 43, 37, 10$. (3) Simulated spectrum with NMR parameters obtained by GIPAW, $\delta_{\text{iso}} = -988$ ppm, $\delta_\delta = -258$ ppm, $\eta_\delta = 0.331$, $C_Q = -41.49$ MHz, $\eta_Q = 0.77$, $\alpha, \beta, \gamma = 61, 45, 27$. 
Figure S7. $^{93}\text{Nb}$ NMR spectra of a stationary powdered sample of SnNb$_2$O$_6$ acquired at 9.4 T. (1) Experimental spectrum. (2) Simulated spectrum using NMR parameters reported in [1] based on the experimental spectra, $\delta_{\text{iso}} = -1010$ ppm, $\delta_0 = 0.0$ ppm, $\eta_0 = 0.0$, $C_Q = 40$ MHz, $\eta_Q = 0.45$, $\alpha,\beta,\gamma = 0,0,0$. (3) Simulated spectrum using NMR parameters obtained by GIPAW, $\delta_{\text{iso}} = -978$ ppm, $\delta_0 = 141$ ppm, $\eta_0 = 0.693$, $C_Q = -32.86$ MHz, $\eta_Q = 0.56$, $\alpha,\beta,\gamma = 124,4,53$. 
Figure S8. 8.5 kHz MAS and stationary $^{93}$Nb NMR spectra of BiNbO$_4$ acquired at 21.1 T and 9.4 T as indicated. (1) Experimental spectra. (2) Simulated spectra with NMR parameters determined in this work from the experimental spectra, $\delta_{\text{iso}} = -977$ ppm, $\delta = -150$ ppm, $\eta_{\delta} = 0.560$, $C_Q = 20.70$ MHz, $\eta_Q = 0.51$, $\alpha, \beta, \gamma = 24, 22, 78$. (3) Simulated spectra using NMR parameters obtained by GIPAW based on the crystal structure, $\delta_{\text{iso}} = -955$ ppm, $\delta = -118$ ppm, $\eta_{\delta} = 0.177$, $C_Q = -21.76$ MHz, $\eta_Q = 0.56$, $\alpha, \beta, \gamma = 0.25, 90$. 
Figure S9. $^{93}$Nb NMR spectra of a powdered sample of La$_3$NbO$_7$ acquired at 21.1 T (left) and 9.4 (right, MAS 35 kHz). (1) Experimental spectrum. (2) Simulated spectrum based on experimental NMR parameters determined in this work, $\delta_{\text{iso}} = -1015$ ppm, $\delta_{\phi} = 113$ ppm, $\eta_\phi = 0.69$, $C_Q = 49$ MHz, $\eta_Q = 0.275$, $\alpha,\beta,\gamma = 50,27,72$. (3) Simulated spectrum using NMR parameters obtained by GIPAW calculations, $\delta_{\text{iso}} = -930$ ppm, $\delta_{\phi} = 153$ ppm, $\eta_\phi = 0.023$, $C_Q = -45.52$ MHz, $\eta_Q = 0.027$, $\alpha,\beta,\gamma = 90,19,0$. 
Figure S10. $^{93}$Nb NMR Te$_3$Nb$_2$O$_{11}$ acquired at 9.4 T (above) and at 20.8 T (below). Static and MAS NMR spectra are shown as indicated. (Upper traces) Experimental spectra. (Middle traces) Simulated spectra using experimental NMR parameters determined in this work, $\delta_{iso} = -1176$ ppm, $\delta_\delta = -320$ ppm, $\eta_\delta = 0.680$, $C_Q = 26.00$ MHz, $\eta_Q = 0.97$, $\alpha, \beta, \gamma = 166, 70, 51$. (Lower traces) Simulated spectra based on GIPAW-calculated NMR parameters, $\delta_{iso} = -1156$ ppm, $\delta_\delta = -306$ ppm, $\eta_\delta = 0.256$, $C_Q = -26.29$ MHz, $\eta_Q = 0.89$, $\alpha, \beta, \gamma = 172, 85, 50$. 

Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics
This journal is © The Owner Societies 2013
Figure S1. Polyhedral representation of the crystal structure of VNb$_9$O$_{25}$. (Panel A) Nb1 octahedra in yellow are shown connected to Nb2 octahedra in gray. (Panel B) Nb2 octahedra in red are shown connected to Nb3 and Nb1 octahedra in gray. (Panel C) Nb3 octahedra in pink are shown connected to Nb2 octahedra in gray and to VO$_4$ tetrahedra in green. Inset on the right shows that each VO$_4$ tetrahedron (green) is connected only to Nb3 octahedra (pink).
Figure S12. Anisotropy of $^{93}$Nb chemical shielding in niobates, $\delta_{\delta}(^{93}\text{Nb})$, as a function of NbO$_x$ coordination number (C.N.). GIPAW-calculated theoretical values are shown as blue squares, while the experimentally determined anisotropy values are shown as yellow circles.
**Figure S2.** Optimized crystal structure of $\text{K}_8\text{Nb}_6\text{O}_{19}$ (below) and the coordination oxygen environment of the three non-equivalent niobium sites in this crystal structure (above).
References
