NMR Crystallography: ^{17}O RT MAS NMR of IO_4^- Ions Reveals $^1J(^{17}O\text{-}^{127}I)$ and its Structure

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Introduction

Recent 21.15 T solid-state ^{17}O VT MAS NMR studies of Cs_2WO_4 & $KMnO_4$ [1] and $KReO_4$ & NH_4ReO_4 [2] show that the ^{17}O MAS spectra of the XO_4 anions for these salts change dramatically at low temperatures compared to the spectra at Room Temperature (RT). This is due to rapid reorientations of the tetraoxoanions at RT in the solid-state which make the oxygens interchange between all four possible positions [1]. Here we present some exciting ^{17}O MAS NMR results obtained at RT for the periodate anions in $NaIO_4$ and KIO_4 which reveal the $^1J(^{17}O\text{-}^{127}I)$ coupling and the crystal structure (NMR crystallography) from analysis of these spectra.

Experimental

^{17}O RT MAS NMR spectra of ^{17}O-enriched (~10%) $NaIO_4$ and KIO_4 were recorded at 19.6 T (112.8 MHz) and partly also at 21.15 T (122.0 MHz), using the NHMFL ultra-narrowbore 830 MHz and 900 MHz ultra-widebore magnets, respectively, and 3.2 mm MAS probes, respectively. All ^{17}O MAS spectra were analyzed using the new XSTARS software recently presented [2].

Results and Discussion

Our recent low-temperature ^{17}O MAS NMR studies of several tetraoxoanions [1, 2] resulted in the first direct observation of a scalar *J*-coupling between two quadrupolar nuclei in solids, i.e., $^1J(^{17}O\text{-}^{187}Re)$ ~ –270 Hz for $KReO_4$ and NH_4ReO_4 [2].

In contrast to our recent low-temperature ^{17}O MAS NMR studies of the two perrhenates [2], the appearance of the RT ^{17}O MAS NMR spectra of $NaIO_4$ (see Figure 1) and KIO_4 are both influenced by the $^1J(^{17}O\text{-}^{127}I)$ coupling, even at RT. Fig. 1 shows a horizontal expansion for the centerband of the ^{17}O MAS NMR spectrum for the central transition at RT (of $NaIO_4$) which illustrates that the two "horns" of the 2nd order quadrupolar-broadened doublet-pattern (C_Q = 11.15 MHz, η_Q ~ 0) appear like "teeth-on-a-saw", because of the $^1J(^{17}O\text{-}^{127}I)$ coupling (^{127}I is a spin I = 5/2 nucleus). As illustrated by the two spectra in Fig. 1, the expected "six-peak" pattern for both "horns" due to the $^1J(^{17}O\text{-}^{127}I)$ coupling appears as a "seven-peak" pattern (incl. the outer-region shoulders) in both the experimental and simulated spectra. Optimized simulated spectra show that the additional splitting into a "seven-peak" pattern is caused by an extremely small and precise value for the ^{17}O asymmetry parameter η_Q = 0.07 (and NOT to a deviation in MAS-angle setting). Furthermore, these optimized simulations reveals that $^1J(^{17}O\text{-}^{127}I)$ is of opposite sign to the dipolar coupling $D(^{17}O\text{-}^{127}I)$ = –600 Hz, i.e., $^1J(^{17}O\text{-}^{127}I)$ = +490 Hz. All experimental results agree with CASTEP calculated values (C_Q = 10.7 MHz, η_Q = 0.08), with an ADF calculated $^1J(^{17}O\text{-}^{127}I)$ = +449 Hz, with the crystal structure of $NaIO_4$ [3] used in these calculations, and that used in the ^{17}O MAS NMR analysis of the similar structure for the ReO_4^- anions [2].

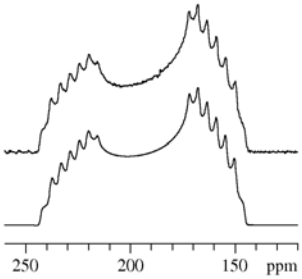

Fig.1. ^{17}O MAS NMR spectrum of $NaIO_4$. Upper: Experiment. Lower: Simulation. (See text).

Conclusions

Analysis of ^{17}O RT MAS NMR spectra of $NaIO_4$ and KIO_4 reveals NMR crystallography for the IO_4^- anion.

Acknowledgements

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References

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