High sensitivity of $^{17}$O NMR to p-d hybridization in transition metal perovskites: first principles calculations of large anisotropic chemical shielding

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College of William and Mary — First principles calculations are used to show that O chemical shielding tensors, $\hat{\sigma}$, are a sensitive indicator of local structure in transition metal ABO$_3$ perovskites, due to their strong dependence on covalent O(2p)-B(nd) interactions. This indicates that $^{17}$O NMR spectroscopy, coupled with first principles calculations, can be an especially useful tool to study the local structure in complex perovskite alloys. Our principal findings are 1) a large anisotropy between deshielded $\sigma_x \simeq \sigma_y$ and shielded $\sigma_z$ components; 2) a nearly linear variation of isotropic $\sigma_{iso}$ and uniaxial $\sigma_{ax}$ components, as a function of the B-O-B bond asymmetry, across all the systems studied; 3) the demonstration that the anisotropy and linear variation arise from large paramagnetic contributions to $\sigma_x$ and $\sigma_y$, due to virtual transitions between O(2p) and unoccupied B(nd) states. 4) Very good agreement with recent BaTiO$_3$ and SrTiO$_3$ single crystal $^{17}$O NMR measurements of isotropic $\delta_{iso}$ and uniaxial $\delta_{ax}$ chemical shifts, and good agreement with PbTiO$_3$ and PbZrO$_3$ powder spectrum $\delta_{iso}$ measurements.

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2Pechkis et al., JCP 131, 184511 (2009); references therein.

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