Figure 1S

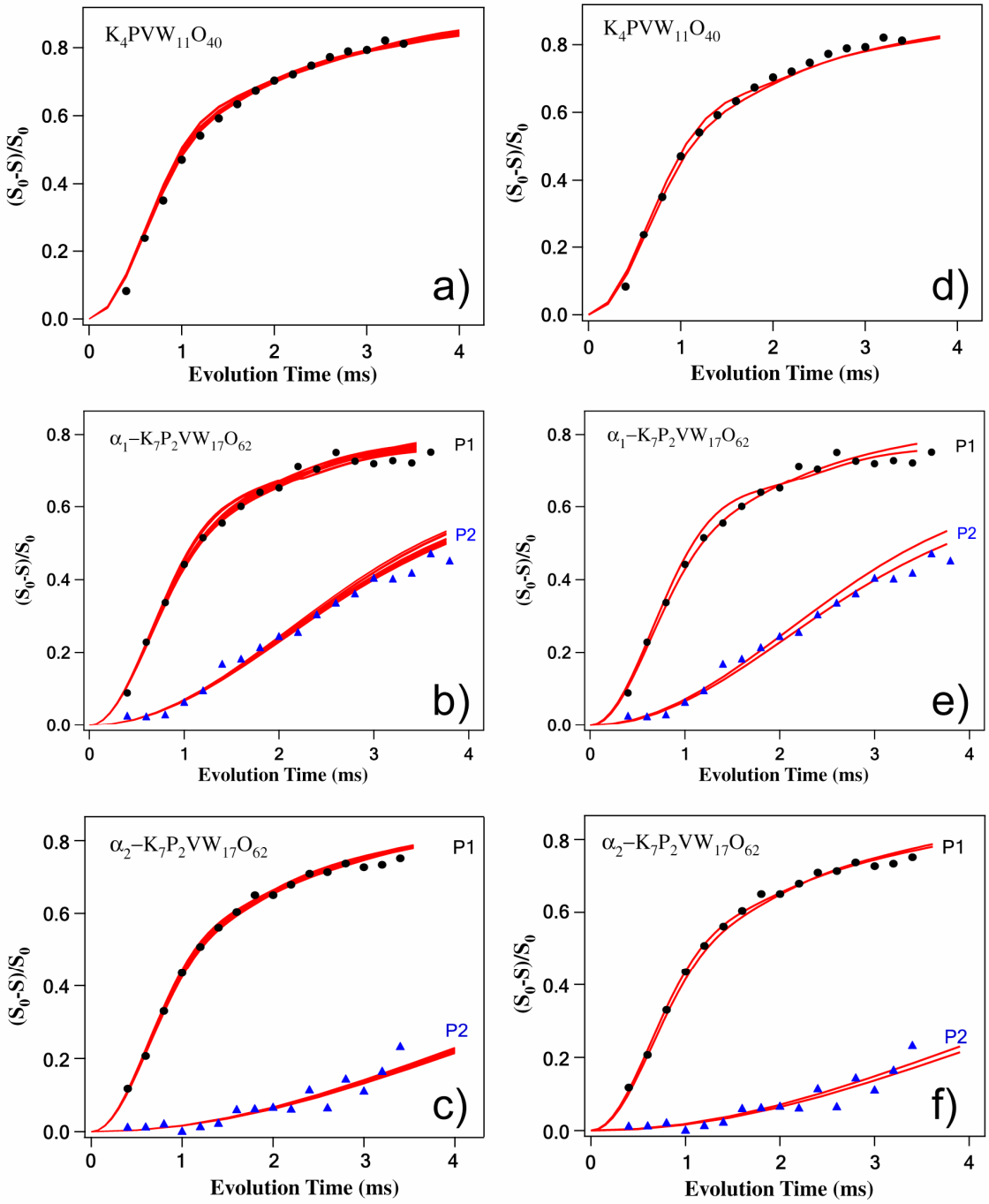

Figure 1S. Left: the experimental data and the simulated REAPDOR dephasing curves using the 52 pairs of polar angles (θ, ϕ) specified in the text, for: (a) $K_4PVW_{11}O_{40}$, (b) 4-$K_7P_2VW_{17}O_{62}$•$17H_2O$, (c) 1-$K_7P_2VW_{17}O_{62}$•$18H_2O$. Right: the experimental data and the minimum and maximum simulated REAPDOR dephasing curves, for: (d) $K_4PVW_{11}O_{40}$, minimum curve simulated using polar angles (90º, 105º) and maximum curve simulated using polar angles (30º, 0º); (e) 4-$K_7P_2VW_{17}O_{62}$•$17H_2O$, P1: minimum curve simulated using polar angles (90º, 120º) and maximum curve simulated using polar angles (30º, 0º), P2: minimum curve simulated using polar angles (60º, 60º) and maximum curve simulated using polar angles (30º, 0º); (f) 1-$K_7P_2VW_{17}O_{62}$•$18H_2O$, P1 and P2: minimum curve simulated with polar angles (90º, 90º) and maximum curve with polar angles (0º, 90º).

2. Error analysis of REAPDOR fraction

In general, if z is calculated as a function $z = f(x, y)$ of x and y, then the propagated error e_z in z is derived from the errors e_x and e_y in x and y according to [1]

$$e_z^2 = \left(\frac{\partial z}{\partial x}\right)^2 e_x^2 + \left(\frac{\partial z}{\partial y}\right)^2 e_y^2$$

These are not relative, but absolute errors.

In our case, the REAPDOR fraction R is calculated as

$$R = \frac{S_0 - S}{S_0}$$

giving

$$\frac{\partial}{\partial S_0} R = \frac{S}{S_0^2}, \quad \frac{\partial}{\partial S} R = -\frac{1}{S_0}$$

If the errors, e, in S and S_0 are the same, then the error in the REAPDOR fraction is therefore

$$e_R = e\frac{\sqrt{S_0^2 + S^2}}{S_0^2} = \frac{e}{S_0}\sqrt{2 + R^2 - 2R}$$

For small REAPDOR fraction, $R = 0$, the error is $e_R = 1.41/\mathrm{SNR}$, where SNR is the signal-noise ratio of S_0. For large fraction, $R = 0.8$, the error is relatively smaller, $e_R = 1.02/\mathrm{SNR}$. However, T_2 relaxation usually causes an increase in e_R at longer evolution times because of a decrease in S_0, unless the number of scans is increased to compensate the effect of relaxation.

[1] See, for instance, P. Gans, Data fittting in the chemical sciences by the method of least squares, Chichester, Wiley, 1992, p. 17.