

Details of the Simulation

The first emission curve (obtained before any Na⁺ was added) was assumed to arise entirely from the free species.

$$I_{\lambda}^f = \text{emission intensity at wavelength } \lambda \text{ for } \mathbf{2} \text{ or } \mathbf{3}$$

The last emission curve (obtained in the presence of a saturating excess of Na⁺; i. e. when the addition of more Na⁺ had no effect on the emission) was assumed to arise entirely from the Na⁺ bound state.

$$I_{\lambda}^b = \text{emission intensity at wavelength } \lambda \text{ for the } \mathbf{2}\text{-Na}^+ \text{ or the } \mathbf{3}\text{-Na}^+ \text{ complex}$$

Now consider an intermediate case, where the solution contains x mol fraction of the **2**-Na⁺ or the **3**-Na⁺ complex (and 1-x mol fraction of free **2** or free **3**). In this case the total emission intensity at any wavelength λ is the weighted average of the emission intensities due to **2** or **3** and the **2**-Na⁺ or **3**-Na⁺ complex respectively. Thus the intensity at wavelength λ is given by:

$$I_{\lambda}^m = (1-x) I_{\lambda}^f + x I_{\lambda}^b \quad \text{..... eq. 1}$$

To calculate the emission curves for **2** and **3**, equation 1 was used. In both cases x was varied from 0.0 to 1.0 in steps of 0.1. The intensity was calculated at 1 nm intervals over the same wavelength range as was used for the first (x = 0) experimentally obtained curve. This generated a set of 9 simulated emission curves which were plotted on the same graph as the first (x=0) and last (x=1) curves which were experimentally obtained.

Figure A shows the experimentally obtained set of emission curves for **3** and Figure B shows the simulated curves for **3**. Note the close parallels between the two.

Figure C shows the experimentally obtained set of emission curves for **2** and Figure D shows the simulated curves for **2**. Note the divergence.







