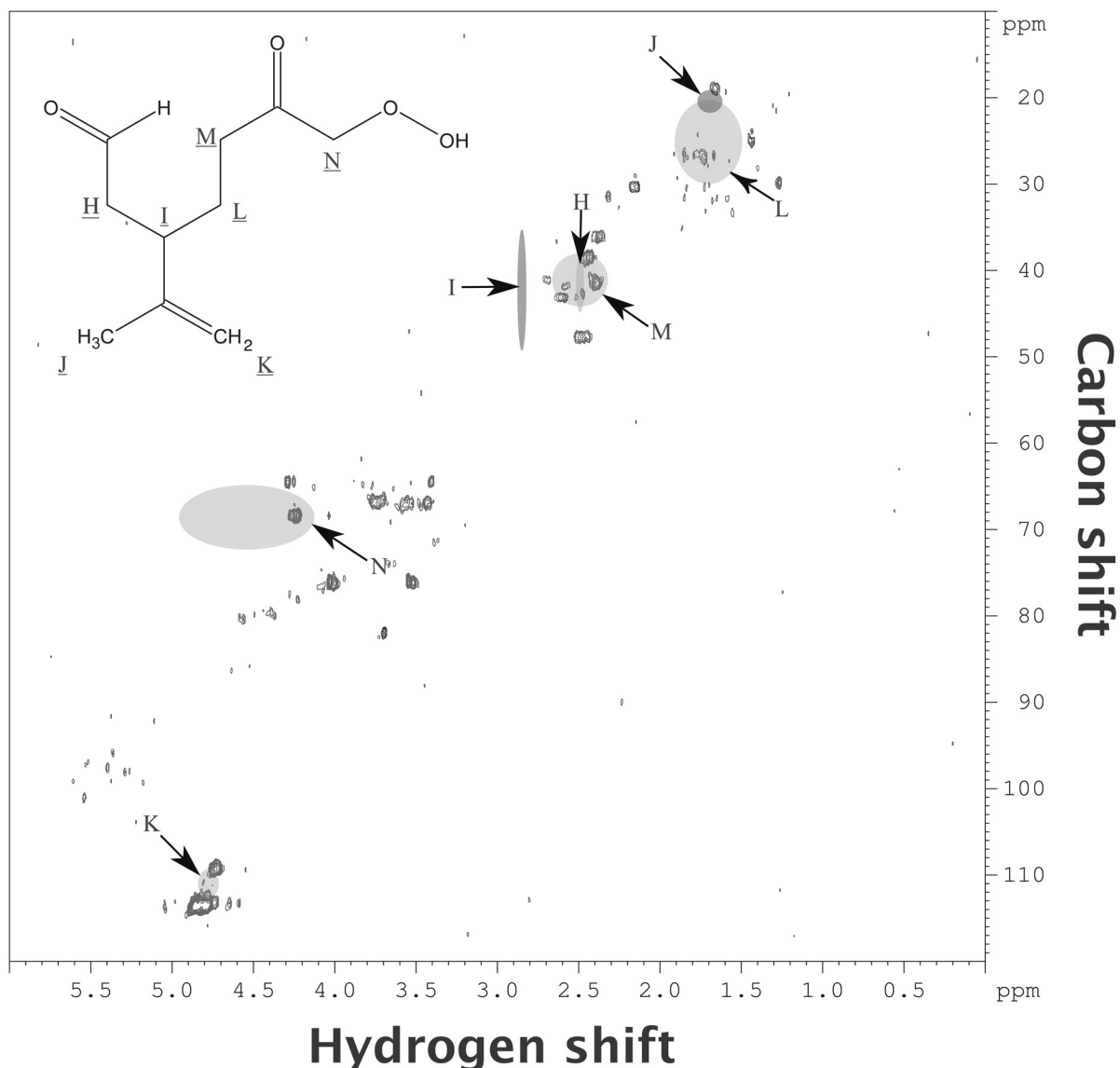


Secondary organic aerosol formation from multiphase oxidation of limonene by ozone: mechanistic constraints via two-dimensional heteronuclear NMR spectroscopy



Example assignment for a 2-D HSQC spectrum obtained under a large excess of limonene. The spectrum for the candidate hydroperoxide was predicted using ACDLab online/ChemSketch 8.0 (<http://www.acdlabs.com>), and the results are shown as colored error ellipses for each of the indicated carbons (H-M). Phase indicates secondary (red) or either primary or tertiary (black) protons. Starting upfield:

The unsaturated methylene is a clear match at K, with good precision in carbon and hydrogen. Note that the unsaturation peak appears off of the general H-C diagonal characteristic of saturated carbons. All spectra show the two peaks separated by about 3 ppm in C shift, indicating some differences in the environment near the double bond. No spectra show any sign of a tertiary unsaturation, indicating that no endocyclic unsaturation remains in the limonene reaction products.

The highly substituted methylene at N is a good match to the strong peak within the error ellipse. The distinctive “box” of peaks remains in all spectra, indicating that the SOA products all contain highly substituted reaction products. The spectra are quite consistent with the substituted hydroperoxide structure shown.

The methyne proton is a good but not perfect match to the weak black peaks at 2.6 ppm H-shift.

The two methylenes H and M adjacent to carbonyl functionalities are an excellent match.

The (lone) unsubstituted methylene L is a good match.

The methyl J is a good match.