PROGRESS MADE TOWARDS CONTEXT-FREE MOLECULAR STRUCTURE DETERMINATION FROM ISOTOPOLOGUE ROTATIONAL SPECTROSCOPY

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Recent algorithms[ab] have demonstrated *context-free* assignment of rotational constants—needing no knowledge of the chemical species other than the rotational spectrum. Efforts to date to subsequently determine molecular structure require further information including assignment of singly-substituted isotopologues[cd], mass spectroscopy[d], and data mining[de]. We investigate two methodologies to resolve sign ambiguities of Kraitchman's substitution coordinates. The first methodology requires candidate rotational constants of doubly-substituted isotopologues. Given many such candidates, we have worked out how to determine 1) which candidates for singly- and doubly-substituted isotopologues are most probable, and 2) doubly-substituted atoms' relative position octant. This is realizable given resolution of doubly-substituted species in natural abundance, which is 10-100x order of magnitude above our instrument's present signal to noise.

The second methodology requires precision measurement of the electric dipole moments and magnetic g-factors of both the parent and singly-substituted isotopologues. The magnetic g-factor is measured via application of a large magnetic field to our microwave spectrometer, as done by Flygare et. al. (1969). For a 6 carbon molecule, this could be realized given the ability to resolve a $\approx 10^{-5}$ percent difference between magnetic g-factors of the parent and singly-substituted isotopolog species, as well as resolve the electric dipole moment to 4 or 5 significant figures. Improving the capabilities of microwave spectrometers to within these thresholds would therefore enable context-free molecular structure determination.

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