IS THE SUBSTITUTION STRUCTURE ACCURATE ?

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Highly precise rotational constants are often used in the substitution method (through Kraitchman's equations) to calculate atomic coordinates with an allegedly marvellous precision. The accuracy of Kraitchman's equations is investigated and it is found that it deteriorates when the mass of the molecule increases, the smallest coordinates being the least accurate as expected, but also coordinates larger than 0.5 Åmight be badly in error. This explains the discrepant results found in the literature for many large molecules. An explanation is provided in the particular case of diatomic molecules. Remedies to this problem are discussed. The mass-dependent methods seem to be a possible solution.