A DEPERTURBATION METHOD TO AID IN THE INTERPRETATION OF ISOTOPIC SPECTRA

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A common approach to the identification of new molecular species is based on the comparison between theoretical predictions and experimental measurements of fundamental vibrational frequencies and their corresponding isotopic shifts. However, these comparisons are not always reliable when vibrational fundamentals are close in frequency. In these cases the symmetry-allowed interactions (couplings) between vibrational modes magnify the sensitivity of the isotopic shift calculations to the full force constant matrix. The study of vibrational spectra of long carbon chains exhibits this problem.

The partial $deperturbation\ method$ presented here is introduced in an attempt to extend the original approach of using theoretical calculations to interpret experimental spectra by analyzing isotopic shifts using perturbation theory. Rather than a direct comparison of fundamental and isotopic shift frequencies, the method makes use of isotopic data for a set of isotopic abundances in order to compare the coupling effects observed in the experimental isotopic shifts with those predicted by perturbation theory. The method completely eliminates the second order contribution to the isotopic shift and thereby diminishes the sensitivity of predicted shifts. The successful application of the method in the correct assignments of the $\nu_4(\sigma_u)$ mode of linear C_7 as well as the $\nu_5(\sigma_u)$ and $\nu_6(\sigma_u)$ modes of linear C_9 is also presented.