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A Deperturbation Method to Aid in the Interpretation of Infrared Spectra GUILLERMO GARCIA, MAGNUS RITTBY, Texas Christian University — Theoretical predictions of fundamental vibrational frequencies of molecules and their corresponding frequency shifts caused by isotopic substitutions are useful in identifying new molecular species. The application of this technique can break down when vibrational fundamentals are close in frequency. The predicted isotopic shifts can then become highly sensitive to the full force constant matrix. Such is for example the case in the study of the vibrational spectra of long carbon chains. The deperturbation method presented here is introduced in an attempt to shed more light on this problem as well as to provide a means to extend the original approach of using predicted isotopic shifts to interpret experimental spectra. Using perturbation theory we show that the second order contribution to the isotopic frequency shift can be completely eliminated when combining data from appropriately selected isotopomers, eliminating the lowest order (near) resonant contribution to the isotopic frequency shift. We present the derivation of the model as well as illustrative examples and comparison with existing experimental data.

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