A MULTISPECTRUM NONLINEAR LEAST SQUARES SPECTRUM FITTING TECHNIQUE: PARAMETERIZATION AND CONSTRAINTS

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Frequently the fitting of molecular spectra is hindered by the fact that known information concerning the spectra is not used in the fitting. This problem is apparent when solving for traditional spectral line parameters in crowded spectra. For example, two spectral lines may be severely blended even on the best resolved spectrum in the solution and thus their spectral line parameters may be highly correlated. Additional information such as the relationship of the spectral line parameters to each other or to other lines in the fit could provide enough information to resolve the needed parameters. Frequently the final objective is to find some parameter such as rovibrational constants, band strength or a specific functional dependence of broadening on a quantum number. A solution for the final parameters rather than those of the spectral lines will have fewer unconstrained parameters and give a better solution. In a multispectrum environment a spectrometer parameter may be unknown and require being part of the solution, but the parameter may be known, for example, to be identical from spectrum to spectrum.

Either the fitting program must be rewritten to address the particular problem encountered or else a poor fit is all that is possible. Generally, the program modifications are specific to only the case at hand. A very general technique for constraining parameters without the need for reprogramming has been devised including techniques for calculating the required derivatives. The user is given a small number of simple functions from which constraints among parameters can be generated. Some examples will be shown in both this presentation and in another paper[a] concerning the analysis of some NO_2 spectra.

[a] D. Chris Benner et al., this symposium