ANALYSIS OF CONGESTED SPECTRA BY TOTAL SPECTRUM FITTING: A STATISTICAL STUDY

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Heavily overlapped, or congested spectra often display much structure but few individual ”lines.” Methods have been devised for analyzing such spectra through nonlinear least squares fitting of the intensity as a function of wavelength or wavenumber. Such Total Spectrum Fitting (TSF) methods are examined statistically for a simple diatomic model and compared with the standard ”measure-assign-fit” (MAF) approach in use since the dawn of spectroscopy. Monte Carlo computations on typically 1000 synthetic spectra at a time verify that the predictions of the variance-covariance matrix are reliable under many circumstances. However in regions where the P and R branches double up, the predicted standard errors in the key spectroscopic constants rise sharply and greatly exceed estimates from the Monte Carlo ensemble statistics. In the same regions, the MAF method actually gives better precision. However, for imperfectly overlapped R and P branches, the MAF standard errors are typically three times larger than the TSF values; moreover, the MAF statistical errors are dwarfed by bias. The TSF approach, while clearly superior in these tests, has a practical drawback: It, too, can give significant bias if the spectra are analyzed with an incorrect model, as illustrated here through calculations employing the wrong function to describe the spectral lineshape.