A global approach to spectral analysis for precision determination of molecular spectroscopic parameters

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Nowadays, environmental monitoring applications require high-quality spectroscopic parameters for a variety of molecules of particular interest, including water and carbon dioxide. To achieve this goal it is necessary to improve experimental techniques, on the one hand, and develop refined procedures of spectral analysis, on the other hand. In particular, when doing nonlinear least-squares fits of experimental spectra with quite sophisticated line-shape models that involve a relatively large number of free parameters, the statistical correlation becomes a relevant issue that limits the achievable precision.

Here, we report on a global analysis procedure to simultaneously fit spectra from a single (and well-isolated) line across a given range of pressures, sharing a number of free parameters, including the Dicke-narrowing parameter, and the pressure broadening and shifting coefficients. Absorption spectra were recorded with an extremely high fidelity using an absorption spectrometer based upon a pair of offset-frequency locked extended-cavity diode lasers, one of them acting as an optical frequency standard.

Two different line shape models were considered: the speed-dependent Voigt (SDV) and speed-dependent Galatry (SDG) profiles, with a hypergeometric dependence of collisional parameters on the molecular velocities in both cases. This strategy has been applied to the shape of the $4_{4,1}$ -> $4_{4,0}$ line of the $H_2{}^{18}O$ $_1+$ $_3$ band, at 1.38 m. By calculating the covariance matrix, we demonstrate that the correlation coefficients can be significantly reduced, as compared to individual fits. For instance, looking at the statistical correlation of the pressure broadening coefficient with the Dicke-narrowing parameter of the SDG profile, it is reduced from 99% down to 37%. Similarly, the correlation coefficient between the broadening and shifting coefficients varies from -30% to +2%.

Therefore, we demonstrate that a precision better than 0.1% can be achieved in the retrieval of spectroscopic parameters of interest.