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Principal and Independent Components Analysis in the context of Molecular Absorption Spectroscopy

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Molecular species of interest very often present overlapping absorption bands both in atmospheric and laboratory spectroscopic data recordings. The separation of these spectra is a prerequisite for quantitative analysis. According to the Beer Lambert Law, the separation of overlapping absorption spectra consists of splitting the observed data into several linear components. If reference spectra are available, the problem can be tackled by Multiple Linear Regression of the observations against the reference spectra, where the unknowns are the respective concentrations of the absorbing species. A widely used technique using this approach is the Differential Optical Absorption Spectroscopy.

Nevertheless, in many cases concentrations and reference spectra are all unknown. The objective of this work is to demonstrate how Principal and Independent Components Analysis are able to extract separated spectra and concentration curves from an unknown mixture of absorbing species. The statistical properties of laboratory data recordings obtained from flash photolysis of I_2+O_3 have been studied to check if the requirements of these two linear decomposition techniques are fulfilled, thus enabling the separation of the spectra of the transient species generated in the system. Results of separation in appropriate spectral windows displaying overlapped vibrational features are presented. As some reference spectra are available, validation is made using conventional Multiple Linear Regression. Apart from the separation of overlapping absorptions, a good result of these techniques in the chemical system studied is the first observation of IO($X^2\Pi_{3/2}$,ν"$\geq$2) in Molecular Absorption Spectroscopy. This fact evidences the ability of these techniques in the recognition of characteristic spectral features.

A combination of Principal and Independent Component Analysis with the principle of Differential Optical Absorption Spectroscopy is also investigated.