

## ***Interactive comment on “Effects of column density on I<sub>2</sub> spectroscopy and a determination of I<sub>2</sub> absorption cross section at 500 nm” by P. Spietz et al.***

### **Anonymous Referee #2**

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#### General comments

Spietz et al. have undertaken a very careful study of the effects of spectrometer parameters and sample column densities on the reliability of laboratory reference spectra used to extract atmospheric I<sub>2</sub> column densities from DOAS measurements. As is well established, the resolution of any spectrometer is of considerable significance when quantitatively studying highly structured regions of a molecular spectrum, such as for I<sub>2</sub> at wavelengths greater than 500 nm. Lab spectra measured at optical densities higher than typical atmospheric conditions are also prone to error because of partial

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saturation of strong absorption lines. These effects are thoroughly investigated using simulations based on existing high-resolution I2 spectra, and reference DOAS spectra at appropriately low column densities are reported. Finally, the paper describes an experimental determination of the I2 absorption cross section at 500 nm, compares this value to other published measurements, and recommends a value with reduced uncertainties.

The importance of having accurate reference spectra for DOAS retrievals of I2 column densities is emphasized by this study, and the authors advocate that DOAS measurements made with instruments with lower resolutions ( $> 1.0$  nm) should use reference spectra obtained with the same spectrometer and similar column density conditions to avoid large systematic errors. These important principles for DOAS will surely apply to many atmospheric molecules other than I2 that also possess highly structured spectra.

#### Specific comments

The paper is long and very detailed, and probably too much so for the amount of new and significant information it contains. There are, for example, extended technical discussions of the discrepancies between other I2 reference spectra and the ones reported here. The text also suffers in places from a lack of clarity. In particular, I did not find the definition of "equivalent optical density" at all clear, and the subsequent arguments were further muddled by a need to distinguish "apparent" from "equivalent" ODs, and the sudden jump on page 5189 to a figure plotted as differential OD (plotted as differential apparent OD / equivalent OD). Do the examples and explanations really need to be so complicated to convey the underlying points?

One conclusion of the analysis is that there may be systematic overestimation of I2 column densities of up to 13%. Tropospheric I2 will have localized sources, and retrieval of local I2 concentrations from DOAS measurements may thus suffer from much larger uncertainties associated with knowing what portion of the DOAS line of sight is actually sampling I2. How significant then is a 13% error in the spectroscopy?

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