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On the impact of Vibrational Raman Scattering of N_2/O_2 on MAX-DOAS Measurements of atmospheric trace gases

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In remote sensing applications, such as the applications of differential optical absorption spectroscopy (DOAS), atmospheric scattering processes need to be considered since they can modify the observed spectra. Inelastic scattering of photons by N_2 and O_2 molecules can be observed as additional intensity, effectively leading to filling-in of both, solar Fraunhofer lines and absorption bands of atmospheric constituents.

The main contribution is due to rotational Raman scattering, which can lead to changes in observed optical densities of absorption lines up to several percent. Measured optical densities are typically corrected for this effect (also known as Ring Effect).

In contrast to that Vibrational Raman scattering of N_2 and O_2 was often thought to be negligible, but also contributes to this effect. We present calculations of Vibrational Raman cross-sections for O_2 and N_2 for the application in passive DOAS measurements. Consequences of vibrational Raman scattering are red-shifted Fraunhofer structures, so called 'Fraunhofer Ghost' lines (FGL), in scattered light spectra and filling-in of Fraunhofer lines, additional to rotational Raman scattering.

We also present first unequivocal observations of FGL at optical densities of up to several 10^4. From our measurements and calculations of the optical density of these FGL, we conclude, that this phenomenon has to be included in the spectral evaluation of weak absorbers. Its relevance is demonstrated in spectral evaluations of Multi-Axis (MAX)-DOAS data and an agreement with calculated scattering cross-sections is found. To exclude cross-sensitivities with other absorbers, such as water vapour, MAX-DOAS data from different latitudes and different instruments were analysed. We evaluate the influence of the additional intensities due to vibrational Raman scattering on the spectral retrieval of IO, Glyoxal, H_2O and NO_2 in the blue wavelength range. In the case of NO_2 the column densities derived from certain wavelength intervals can underestimate the true tropospheric NO_2 concentrations by several 10 ppt if vibrational Raman scattering is neglected in the evaluation. For all absorbers in the blue wavelength range, a reduction of the measurement error is observed, whenever vibrational Raman scattering is explicitly considered, although the obtained column densities for IO, Glyoxal and H_2O are only slightly affected, with differences of less than 20% and typically below their respective detection limits. Estimates on the expected optical densities for other spectral regions are given.