3 µm water vapor self- and foreign-continuum: New method for determination and new insights into the self-continuum

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Determination of H2O continua in the past

Method
- Transmittance spectra from FTS, absorption coefficients from CRDS
- Calculation of H2O local lines using mostly HITRAN parameters
- Only use troughs, subtract local line contributions

Disadvantages (especially for FC)
- Large gaps
- Low resolution
- Errors due to inadequacy of line parameter database
New method for H2O continuum determination

Method
• Usage of same spectra for line parameter and continuum determination
• Continuum extracted from fitted baseline from microwindow-based multispectrum fit

Advantage
• Continuum information not constrained to troughs – only few gaps
• Local line errors small
• Sufficient spectral resolution – determined by microwindow width, baseline = polynomial, degree $\leq 2$
• Advantage is largest for in-band FC

Prototyping
• Water measurements between 1800 and 4000 cm$^{-1}$ with high quality line parameters already determined [Loos2017;Loos2017a]
Since 1990 high resolution spectroscopy for spectroscopic databases of atmospheric constituents
Commercial Bruker IFS125 HR FT spectrometer 10-40000 cm⁻¹
Multireflection cell

- 14-165 m absorption path, accuracy 0.1%
- 190-350 K temperature range
- Mirrors actively thermalized
- 0.1 K temperature homogeneity
- Attached to Bruker IFS 125 HR
- Transfer optics in sample chamber
- Mirror coating selected for minimum reflection loss
Other infrastructure: Gas handling

- Precision pressure transducers: mks Baratron 0.05% accuracy
- Temperature sensors: Lakeshore Pt100, 0.1 K accuracy
- 800 l stainless steel gas mixing chamber, stirrer
- Flow and pressure controllers
Multispectrum fitting software
Multispectrum fit of pure H2O spectra
Multispectrum fit of air-broadened H2O spectra
Measurements used for continuum determination

- SC \propto p_{H_2O}^2 \cdot l = IC_s
- FC \propto p_{H_2O} \cdot p_{air} \cdot l = IC_f

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Transmittance contributions of pure H2O spectra
green: observed, red: pure line spectrum, black: baseline
Transmittance contributions of air-broadened H2O spectra
green: observed, red: pure line spectrum, black: baseline
Self-Continuum multispectrum fit to baselines
black: observed, red: calc, green: OMCx10
Foreign-Continuum multispectrum fit to baselines
black: observed, red: calc, blue: SC contribution, yellow: FC contribution, green: OMCx10
Validation of SC with air-broadened measurements

![Graph showing SC from air-broadened spectra, SC from self-broadened spectra, and 10 x uncertainty.](image)
Comparison of SC with CAVIAR
lower traces: continua, upper traces: uncertainties/differences x 4, zero blue line. Black: present work, green: CAVIAR, red: CAVIAR – present work
Comparison of FC with CAVIAR and MT_CKD3.2

![Graph comparing FC, CAVIAR, and MT_CKD3.2 models across different wavenumbers.](image-url)

- **FC - Lorentz wings > 100 cm\(^{-1}\)**
- **FC + base term + wing corr.**
- **MT_CKD3.2**

**C\(_f\)/\(cm^2\text{molec}^{-1}\text{atm}^{-1}\)**

**Wavenumber/cm\(^{-1}\)**
Shape of self-continuum

- H2O-dimer dissociating into monomer
- Spectrum in between bound dimer and monomer
- Ab initio can calculate spectra but high energy level density close to dissociation limit

- Simpler approach: Bound dimer + quasibound dimer
- Quasibound dimer has shape of monomer band but large broadening due to short lifetime (FWHM=14-40 cm⁻¹, Ptashnik, 2011).
- New concept for estimating bound dimer spectrum: Generic band shapes of parallel and perpendicular rovibrational bands
Shape of bound dimer bands

- Strongest vibrational fundamentals in 3 µm region from ab initio/experiments:
  - symmetric OH stretch of the donor H₂O: \( \nu_3 \)
  - antisymmetric OH stretch of the donor H₂O: \( \nu_1 \)
  - antisymmetric OH stretch of the acceptor H₂O: \( \nu_9 \)
- Ground state rotational constants: \( A \approx 7 \text{ cm}^{-1} \), \( B \approx C \approx 0.2 \text{ cm}^{-1} \)
Shape of bound dimer bands

- Ptashnik: All bands have Lorentzian shape with 60 cm\(^{-1}\) FWHM
- New approach: Generic band shapes of parallel and perpendicular bands of symmetric top
- \(\nu_3, \nu_1\): dipole moment changes parallel and perpendicular to A-axis, \(\nu_9\): perp.
- Effects smearing band structure: diff. rot. const. in ground and excited vib. states, centrifugal distortion, hot bands (ca. 85% of total intensity), asymmetry splitting, torsional tunneling splitting, lifetime broadening, Cave: floppy molecule
- FWHM parallel band rovibrational lines: 5 cm\(^{-1}\), perpendicular band 10 cm\(^{-1}\)
Fit of SC continuum

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Wavenumber/cm$^{-1}$

- exp
- calc
- bound
- quasi-bound

$CS/(cm^2\text{molec}^{-1}\text{atm}^{-1})$

$K_{Db}$, $K_{Dq}$, $K_{eq}$, $f_{S_{v3}}$, $f_{S_{v1}}$, $f_{S_{v9}}$, $f_{para_{v3}}$, $f_{para_{v1}}$, $\nu_{0,v3}$, $\nu_{0,v1}$, $\nu_{0,v9}$, FWHM qD

$lit$ values: 0.052, 0.55(8), 0.28(6), 0.18(3)

$fit$ values: 0.025, 0.042, 0.067, 0.48, 0.27, 0.25, 0.54, 0.6, 3610, 3724, 3749, 20
Conclusion

• New method for H2O in-band continuum determination prototyped, using same spectra for line parameters and continuum
• Example: FC and SC in 3 µm region
• Continua show better spectral coverage and resolution, and smoothness
• SC in good agreement with CAVIAR work
• FC in agreement with CAVIAR work, showing P-, Q-, and R-branch
• SC was fitted applying bound and quasibound dimer contributions
• Rovibrational bands of bound dimer were simulated by generic parallel and perpendicular symmetric top bands
• Two double peaks in SC can be modelled with parallel rovibrational bands
• Dimer band positions and strengths are in reasonable agreement with theoretical work