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# Observation of ClO, $HO_2$, HOCl, and BrO by ISS/JEM/SMILES

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## Abstract

The Superconducting Submillimeter-Wave Limb-Emission Sounder (SMILES) onboard the International Space Station provided global measurements in the middle atmosphere from 12 October 2009 to 21 April 2010. We present current status of L2 (ClO, HO2, HOCl and BrO), their validation, diurnal variation and other scientific results, using JAXA L2 v2.4 datasets.

## Acknowledgement

The authors appreciate the following project teams to provide the data which need to prepare for this study: Aura/MLS, Envisat/MIPAS-IMK, Odin/SMR, SD-WACCM and MIROC3.2-CTM.

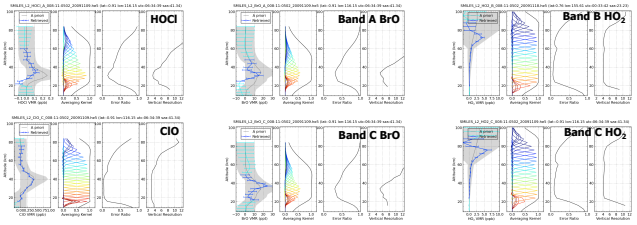
## 1. SMILES measurements

SMILES measured the Earth's limb using the 4-K cooled Superconductor-Insulator-Superconductor (SIS) mixer (Tsys~340K) from 12 October 2009 to 21 April 2010. Critical failure of the submillimeter local oscillator terminated the SMILES observation. SMILES nominally covered latitudes from 38°S to 65°N on each orbit within a 93-minute period. The ISS is not in a sun-synchronous orbit and its orbital plane rotates every ~60 days, so SMILES covered all local times within ~30 days. The total number of scans per day was about 1,600. SMILES has three specified detection bands within the submillimeter-wave region: 624.32–625.52 GHz (Band A), 625.12–626.32 GHz (Band B), and 649.12–650.32 GHz (Band C). Since the instrument contained two sets of acousto-optical spectrometers, two of the three detection bands were measured simultaneously. Table 1 shows species observed in Bands A-C.

Table 1 Species measured by SMILES

| | |
|---|---|
| Band A | $O_3$, $H^{37}Cl$, HOCl, $^{81}BrO$, $HNO_3$, $CH_3CN$, $O_3$ isotopes |
| Band B | $O_3$, $H^{35}Cl$, $HO_2$, $O_3$ isotopes (asym-18, sym-17) |
| Band C | $^{35}ClO$, $HO_2$, $HNO_3$, $^{81}BrO$, $O_3$ isotopes (asym-18, asym-17) |

Figure 1 shows examples of single retrieved profiles, avetraging kernel, error ratio (S/Sa) and vertical resolution of Band A HOCl and BrO, Band B $HO_2$, BandC ClO, BrO and $HO_2$.




Figures 1. Examples of SMILES Band A HOCl (top-left), BrO (top-middle), Band B $HO_2$(top-right), Band C ClO (bottom-left), BrO (bottom-middle) and HO2 (bottom-right) single scan profile, averaging kernel, error ratio (S/Sa) and vertical resolution.

## 2. ClO

SMILES ClO showed minor bias, which should be corrected by using night time mean value (below 35 km, and above 68 km using day time value). Diurnal variation agreed with SD-WACCM below 43 km, but SD-WACCM is ~50% higher than SMILES above 52 km. Validation with daytime Aura/MLS and Odin/SMR showed good agreement over useful range, but IMK-MIPAS is lower than SMILES (not shown here). Comparison with day and nighttime SD-WACCM showed excellent agreement up to 50 km, but it is 50 % higher above 50 km. After correcting bias value, SMILES ClO agreed excellently with SD-WACCM from 22 to 34 km at all latitude regions, which looks confirmed VSLS Cly estimation (~0 ppt).

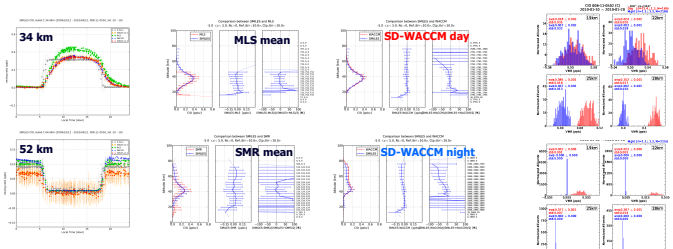
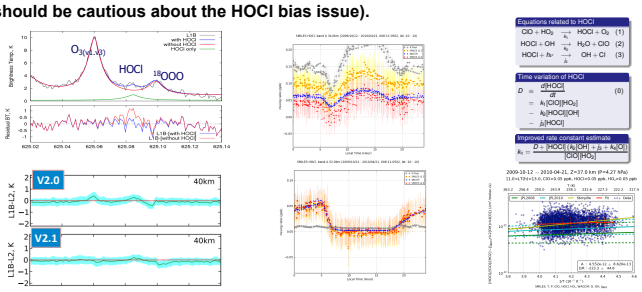



Figure 2. Diurnal variation of ClO at 34 and 64km, Validation with Aura/MLS and Odin/SMR, Comparison with day-night SD-WACCM, and Day-Night ClO histogram of SMILES and SD-WACCM (left to right).

## 3-1. HOCl

HOCl is measured at 2 spectral positions in Band A. Figure shows stronger lines, but it exist on the slope of $H^{35}Cl$ line and overlapped by the $O_{3(v1,v3)}$ and $^{18}OOO$ lines. The frequency tuning (HITRAN to JPL) made better spectral fitting (from v2.0 to v2.1). For the L2 v2.4 new frequency measurement result for $O_3$ and its isotopes have been applied but it showed no significant change to L2 value. L2 v2.4 HOCl apparently became worse than v2.3 due to new L1B non-linearity correction. At the lower altitude region (34 km), HOCl value loooks to be affected by the bias. The reaction rate of ClO + $HO_2$ → HOCl looks to be close to JPL2011 using SMILES ClO, HO2, and HOCl (we should be cautious about the HOCl bias issue).




Figures 3. Band A HOCl signal at 40 km and improvement of spectral fitting from v2.0 to v2.1 (left), Diurnal variation at 34 and 52 km (middle), and Arrhenius plot for the reaction rate of ClO + HO2 → HOCl at 37 km (right).

## 3-2. BrO

BrO is measured Band A and C. Both A and C BrO have significant bias below 37 km. We have been recommending to use Band C BrO due to strong bias of Band A BrO, but if bias correction is made correctly using night time mean value, it looks both A and C are usable. L2 v2.4 showed more bias compared to previous versions due to the new L1B non-linearity correction scheme introduced in the v2.4 (which will be abandoned in the next L2 version). Diurnal variation is slightly different from SD-WACCM, but a priori sensitivity should be checked for SMILES. SMILES has sensitivity to night time BrO up to 65 km. Comparison with SD-WACCM showed a difference since SD-WACCM had no VSLS $Br_y$ for current calculations. Validation with Aura/MLS agreed with MLS error bar. Stachnick et al comparison with their balloon, SMILES and other measurement, and good agreements have reported. They estimated VSLS Bry to be ~6 ppt. As shown in figures, SMILES BrO is slightly less than JPL Balloon measurement, and zonal mean BrO calculated by SD-WACCM has visible variation. The SMILES VSLS Bry estimation by using SD-WACCM Bry/BrO gave ~4 ppt for both Band A and C at all latitude bins and all seasons.

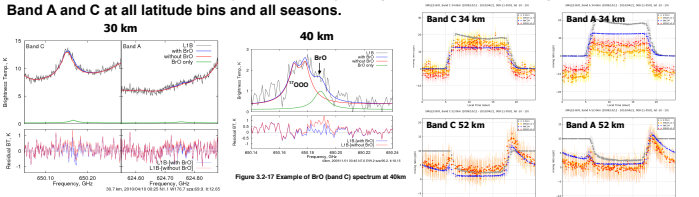
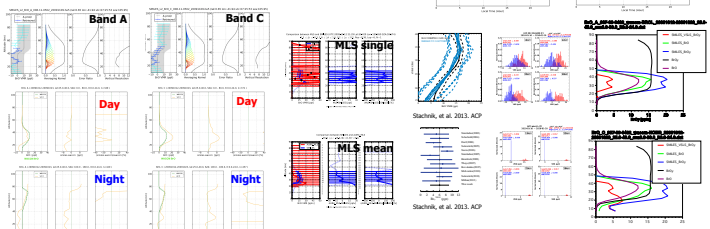


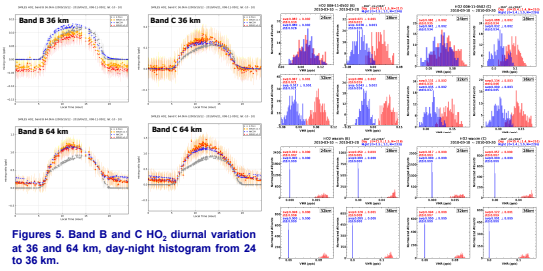

Figure 3.2-17 Example of BrO (band C) spectrum at 40km




Figures 4. Upper panel: Spectral fitting of Band C and A at 30 km, Band C at 40km, Band C diurnal variation at 34 and 52 km, and same for Band A (left to right). Lower Panel: Averaging kernel and comparison with SD-WACCM day and night Band A, Band C, validation with Aura/MLS 3.3, validation with JPL Balloon and their VSLS $Br_y$ estimation, and VSLS $Br_y$ day-night histogram of SMILES and SD-WACCM, estimation VSLS $Br_y$ using SMILES BrO and SD-WACCM $Br_y$/BrO. (left to right)

## 3-3. $HO_2$

$HO_2$ also shows significant bias below 40 km, which can be corrected by subtracting nighttime mean value. Band B showed larger bias because of the interference by the O3 and H35Cl lines. After the bias correction, agreements with SD-WACCM looks reasonable (SMILES is +0~10%) both Band B and C over 32-64 km. Above 68 km SMILES HO2 is larger than SD-WACCM, one possibility is $H_2O$ value in SD-WACCM.




Figures 5. Band B and C $HO_2$ diurnal variation at 36 and 64 km, day-night histogram from 24 to 36 km.

Table 2 Zonal mean $HO_2$

| km | SMILES | SD-WACCM |
|---|---|---|
| 28 | 57, 56 | 59, 57 |
| 32 | 84, 96 | 96, 94 |
| 36 | 129, 125 | 126, 121 |
| 40 | 180, 192 | 172, 167 |
| 44 | 241, 273 | 239, 234 |
| 48 | 337, 359 | 307, 303 |
| 52 | 384, 419 | 374, 370 |

SMILES is bias corrected (day – night).