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Observed and modeled HOCl profiles in the midlatitude stratosphere: Implication for ozone loss

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[1] Vertical profiles of stratospheric HOCl calculated with a diurnal steady-state photochemical model that uses currently recommended reaction rates and photolysis cross sections underestimate observed profiles of HOCl obtained by two balloon-borne instruments, FIRS-2 (a far-infrared emission spectrometer) and MkIV (a mid-infrared, solar absorption spectrometer). Considerable uncertainty (a factor of two) persists in laboratory measurements of the rate constant (k_1) for the reaction $ClO + HO_2 \rightarrow HOCl + O_2$. Agreement between modeled and measured HOCl can be attained using a value of k_1 from Stimpfle et al. (1979) that is about a factor-of-two faster than the currently recommended rate constant. Comparison of modeled and measured HOCl suggests that models using the currently recommended value for k_1 may underestimate the role of the HOCl catalytic cycle for ozone depletion, important in the midlatitude lower stratosphere. **Citation:** Kovalenko, L. J., et al. (2007), Observed and modeled HOCl profiles in the midlatitude stratosphere: Implication for ozone loss, *Geophys. Res. Lett.*, *34*, L19801, doi:10.1029/2007GL031100.

1. Introduction

[2] One of the main halogen catalytic cycles for ozone loss in the midlatitude lower stratosphere is the HOCl (hypochlorous acid) cycle [*Johnson et al.*, 1995]. Accurate knowledge of the rate constant (k_1) for formation of HOCl,

$$ClO + HO_2 \rightarrow HOCl + O_2, \tag{R1}$$

the rate-limiting step of ozone loss by this cycle, is needed to quantify the contribution to ozone loss by this cycle. However, laboratory measurements of k_1 show a factor-of-two discrepancy for stratospheric temperatures [*Sander et al.*, 2006].

[3] Since (R1) is the only significant gas-phase production mechanism for stratospheric HOCl, model calculations of HOCl should be sensitive to the value of k_1. Here we compare balloon-borne measurements of vertical profiles of HOCl with model calculations to assess the level of agreement for various values of k_1. We focus on the 20 September 2005 midlatitude flight launched from Ft. Sumner, NM (34°N). Several other midlatitude flights are also examined.

2. Kinetics

[4] Figure 1 shows the large discrepancy in laboratory measurements of the rate constant k_1. The JPL 2000 value for k_1 (dotted red) [*Sander et al.*, 2000] was based on five laboratory studies. *Stimpfle et al.* [1979] (dashed green) was the only study conducted at other than room temperature (T), and found a negative T dependence with a non-Arrhenius shape. This study used discharge flow/laser magnetic resonance at pressures (p) of 0.8 to 3.4 Torr. The JPL 2000 expression for k_1 assumed an Arrhenius shape, with a room-T value equal to the mean of the five measurements, and a T dependence similar to that of *Stimpfle et al.* [1979]. Previous ozone assessment models [*World Meteorological Organization*, 2003] used this value for k_1.

[5] The JPL 2006 recommendation for k_1 [*Sander et al.*, 2006] is shown by the solid blue line. Current ozone assessment models [*World Meteorological Organization*, 2007] use this slower value for k_1. Three recent laboratory studies (black lines) led to the revised recommendation, which effectively halves k_1 for stratospheric T. These studies show a range of T dependences, from positive to negative. Even though these new laboratory studies were done under different experimental conditions, such as total p, source chemistry for ClO and HO_2 radical production, and detection technique, the disparate results show no evident correlation with experimental conditions. For example, *Nickolaisen et al.* [2000] (flash photolysis/ultraviolet absorption technique at 50 to 700 Torr N_2) found a rate constant about four times that of Laszlo et al. (plotted by *Nickolaisen et al.* [2000]) (discharge flow/mass spectrometry technique at 1 Torr). While this disparity might at face value be indicative of a p-dependent rate constant (faster at higher pressure), the low-p studies of both *Knight et al.* [2000] (discharge flow/mass spectrometry technique at 1.1 to 1.7 Torr) and *Stimpfle et al.* [1979] are inconsistent with this interpretation.

[6] A more recent measurement of the rate constant for HOCl has been performed [*Hickson et al.*, 2007] which, for stratospheric temperatures, falls in between the JPL 2000 and JPL 2006 values. Within the 1σ uncertainty of this measurement, the value agrees with both JPL 2000 and JPL 2006 for stratospheric temperatures. The implications of this measurement are discussed below.

[7] Several theoretical studies have assessed the expected T and p dependence of k_1 [*Xu et al.*, 2003, and references therein]. The reaction appears to proceed mainly through

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direct H-atom abstraction via a ClO-HO_2 hydrogen-bonded complex on a triplet surface, with formation of HOCl expected to lead to a strong negative T dependence for k_1. A secondary mechanism involves formation and stabilization of an HOOOCl intermediate on a singlet surface, which could lead to a p dependence for k_1.

3. Field Measurements of HOCl

[8] Observations of HOCl were obtained with two balloon-borne, remote-sensing, Fourier Transform Spectrometers. FIRS-2 (Far InfraRed Spectrometer 2) [*Chance et al.*, 1996] measures atmospheric thermal emission in the far-IR (8 to 125 μm). HOCl rotational transitions are probed because they offer higher precision and accuracy than vibrational transitions. Spectra are obtained throughout day and night. These spectra are used to simultaneously retrieve vertical profiles of 28 species, including HOCl and its precursor HO_2. Other species retrieved by the FIRS-2 spectrometer relevant here include O_3, HCl, $ClONO_2$, H_2O, and N_2O.

[9] MkIV [*Toon*, 1991] measures solar absorption over the entire mid-IR (1.8 to 15.4 μm), thus probing vibrational transitions. Spectra are obtained at sunrise and sunset. Vertical profiles are simultaneously retrieved for many species, including HOCl. Other retrieved species relevant here include O_3, HCl, $ClONO_2$, H_2O, CH_4, CO, C_2H_6, and N_2O.

[10] Retrievals for both instruments were run with the latest version of the database of spectroscopic constants, HITRAN 2004 [*Rothman et al.*, 2005]. This version incorporates new measurements of HOCl line intensities and air-broadened linewidths, causing mid-IR line intensities to decrease by about 60% compared to the previous version of HITRAN. As a result, MkIV retrievals are increased by ~60% while FIRS-2 retrievals are increased by only ~10% (see auxiliary material[1]). For the FIRS-2 retrieval of HOCl, the systematic uncertainty, determined by the uncertainty in the broadening coefficient, is estimated to be about 10%. For the MkIV retrieval, the systematic uncertainty, dominated by the uncertainties in HOCl line intensities, is also estimated to be about 10%. Measurement precision is represented by error bars in the figures (see captions).

[11] Both MkIV and FIRS-2 retrievals are regularized using a smoothing constraint. The altitude resolution is ~2–3 km for MkIV, 3 km for FIRS-2. For sunset measurements, we tested whether the assumed variation of HOCl with solar zenith angle along the limb path affects the retrieval. The effect is negligible, $\leq$1% for $p < 20$ hPa, and <5% for higher p.

4. Photochemical Model

[12] We use a photochemical model [*Chance et al.*, 1996; *Sen et al.*, 1999] to calculate profiles of HOCl for conditions encountered during the field measurements. The model also calculates the concentrations of other radical species responsible for ozone destruction, such as ClO and HO_2, as well as numerous reservoir gases. The model assumes diurnal steady state, i.e., that production and loss rates for each species are equal when integrated over a 24-hour period. Photolysis rate coefficients are calculated using a radiative transfer code that accounts for Rayleigh scattering, based on measured profiles of O_3, T, and p.

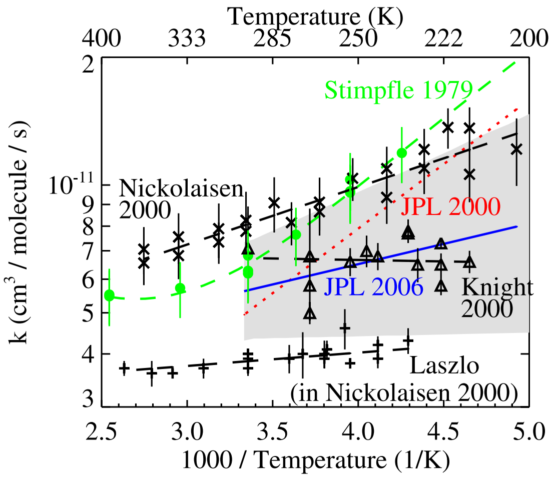

Figure 1. Laboratory measurements of the rate constant, k_1, for the reaction ClO + HO_2 → HOCl + O_2. The current JPL 2006 recommendation is shown by the solid blue line, with the uncertainty shown by the light gray region. The JPL 2000 recommendation is shown by the dotted red line. The four T-dependent measurements considered in JPL 2006 are also shown: the fastest, *Stimpfle et al.* [1979], in green, and three more recent measurements in black. Not shown are the four room-T studies that were also considered in JPL 2006 (references given by *Sander et al.* [2006]).

[13] The simulations of HOCl corresponding to each field measurement primarily use constraints from the specific spectrometer. Profiles of model input total inorganic chlorine (Cl_y), odd nitrogen (NO_y), and total inorganic bromine (Br_y) are obtained from profiles of N_2O measured by each instrument, using well-established tracer relations [*Chance et al.*, 1996; *Sen et al.*, 1999]. Profiles of T, O_3, and H_2O, are available from each instrument. Since only the MkIV spectrometer measures CH_4, MkIV profiles from either the same or nearby flights are used as model input when simulating conditions sampled by FIRS-2. The surface area of sulfate aerosol is based on satellite observations [*Thomason et al.*, 1997], updated to the time of measurement.

[14] Three simulations are conducted for each field measurement, differing only in the value of the rate constant, k_1, for formation of HOCl. The first run, $k_1^{JPL2006}$, uses the JPL 2006 value (slowest). The second run, $k_1^{JPL2000}$, uses the JPL 2000 value (intermediate). The third run, $k_1^{Stimpfle}$, uses the *Stimpfle et al.* [1979] value (fastest).

5. Comparison of Modeled and Observed HOCl

[15] Figure 2 compares observations of HOCl obtained at 34°N on 20 September 2005 with results of three model runs. The FIRS-2 profile of HOCl (Figure 2a) was measured in the early afternoon, when HOCl is near its daily maximum. The MkIV profile (Figure 2b) was measured at sunset, when HOCl is near its minimum. Model results are shown for the same local solar times as the measure-

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[1] Auxiliary materials are available in the HTML. doi:10.1029/2007GL031100.

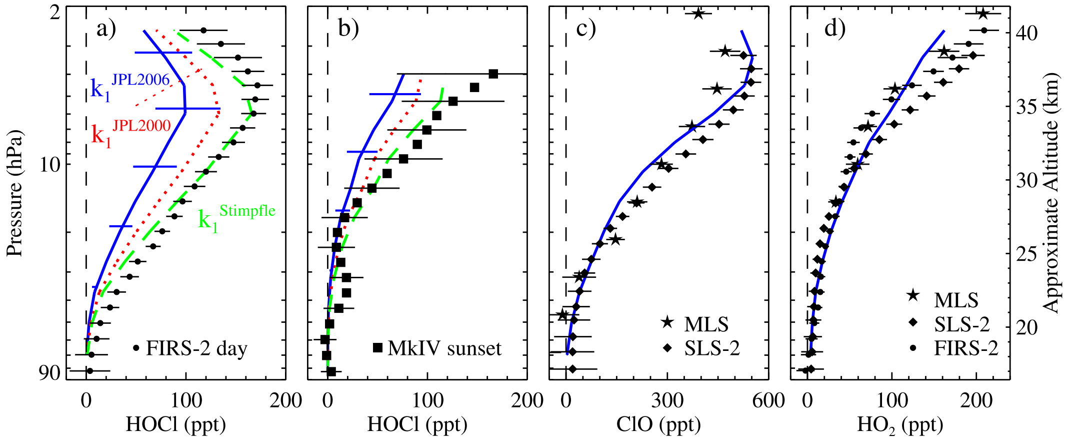

Figure 2. Comparison of observed and modeled vertical profiles for the 20 September 2005 midlatitude balloon flight. HOCl obtained by (a) FIRS-2 and (b) MkIV, respectively. Uncertainties are 1σ estimates of measurement precision. Three model runs for each data set are shown; all use JPL 2006 kinetics, differing in the value of the rate constant, k_1, as indicated. Modeled and measured HOCl precursor profiles, (c) ClO and (d) HO_2.

ments. Profiles obtained by both instruments agree best with the model that uses the fast rate constant, $k_1^{Stimpfle}$.

[16] We note, however, that MkIV measurements of HOCl obtained using the older HITRAN 2000 spectroscopy are lower than those using HITRAN 2004. For the older spectroscopy, best agreement with MkIV is found using the $k_1^{JPL2000}$ model (see auxiliary material).

[17] The blue error bars on the $k_1^{JPL2006}$ run in Figure 2 indicate the uncertainty in the calculated profile of HOCl due to uncertainties in the HOCl production and loss mechanisms other than (R1):

$$\text{(R2)} \qquad HOCl + h\nu \rightarrow Cl + OH$$

$$\text{(R3)} \qquad HOCl + O \rightarrow OH + ClO$$

$$\text{(R4)} \qquad HOCl + OH \rightarrow H_2O + ClO$$

$$\text{(R5)} \qquad HOCl + HCl(aerosol) \rightarrow H_2O + Cl_2$$

$$\text{(R6)} \qquad ClONO_2 + OH \rightarrow HOCl + NO_3$$

$$\text{(R7)} \qquad ClONO_2 + H_2O(aerosol) \rightarrow HOCl + HNO_3$$

We calculated the sensitivity of HOCl to the JPL 2006 uncertainties for these rate constants and photolysis coefficients, first increasing and then decreasing the value of each parameter by its uncertainty, each time calculating the resulting HOCl profiles, and then calculating the square root of the sum of the squares (RSS) of the fractional differences between the resulting HOCl profiles and the original profile. The uncertainty in modeled HOCl is dominated by the uncertainty in the HOCl photolysis coefficient (R2), as well as, for higher altitudes, the uncertainty in the rate of HOCl + O (R3). The error bars in Figure 2 demonstrate that these uncertainties cannot account for the discrepancy between the observed HOCl profiles and the profiles calculated by the $k_1^{JPL2006}$ run.

[18] Measured and modeled profiles of the HOCl precursors ClO and HO_2 are also shown in Figure 2. The balloon-borne SLS-2 (Submillimeterwave Limb Sounder) instrument is a heterodyne radiometer that measures thermal emission spectra near 640 GHz (as described by *Stachnik et al.* [1992], but with a more sensitive, cooled receiver). The SLS-2 measurements (diamond) of ClO and HO_2, as well as the FIRS-2 measurements (circle) of HO_2, were obtained from instruments flown on the same balloon gondola. The satellite-borne MLS (Microwave Limb Sounder) [*Waters et al.*, 2006] measurements (star) represent a monthly zonal mean of version 2.2 data for September 2005 from 30°N to 40°N. Profiles of ClO and HO_2 are insensitive to k_1 because the ClO + HO_2 reaction is a minor loss mechanism for both. The good overall agreement of measured and modeled ClO and HO_2 demonstrates that the ~factor-of-two discrepancy between measured and modeled HOCl for the $k_1^{JPL2006}$ run is not due to errors in the model representation of HOCl precursors (see auxiliary material).

[19] The diurnal variation of HOCl is illustrated in Figure 3 for observations obtained by FIRS-2 (circle) and MkIV (square; data only at sunrise and sunset). For the two pressures shown, the MkIV and daytime FIRS-2 observations are in excellent agreement with the $k_1^{Stimpfle}$ simulation. Measured and modeled diurnal variations of ClO and HO_2 are also in good agreement. While the FIRS-2 sunset measurement of HOCl at 4.6 hPa is low compared to both the $k_1^{Stimpfle}$ simulation and the MkIV observation, this data point agrees (just barely) with the MkIV observation within the uncertainties of the two measurements. Since this is the only flight to date for which FIRS-2 sunset data were obtained, no conclusions can be drawn from this data at this time. Future flights will investigate the behavior of HOCl near sunset in more detail.

[20] Figure 4 shows the results of analyses of several midlatitude flights spanning over a decade of measurements. The difference between observed and modeled HOCl is averaged over all profiles of those mid-latitude flights, for FIRS-2 daytime profiles (Figure 4, left), FIRS-2 nighttime

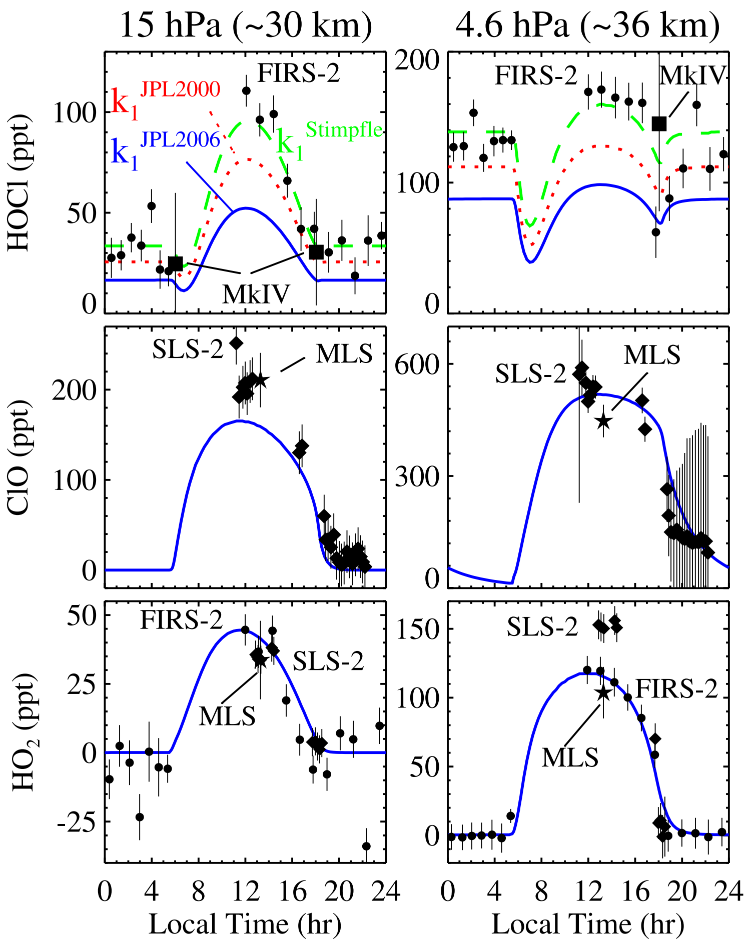

Figure 3. (top) The observed HOCl diurnal variation for the 20 September 2005 flight, for two pressures (15 hPa and 4.6 hPa), as obtained by FIRS-2 (circle). Model runs as in Figure 2. Also shown are MkIV measurements (square). The same comparison for the HOCl precursors (middle) ClO and (bottom) HO_2; measurements as in Figure 2.

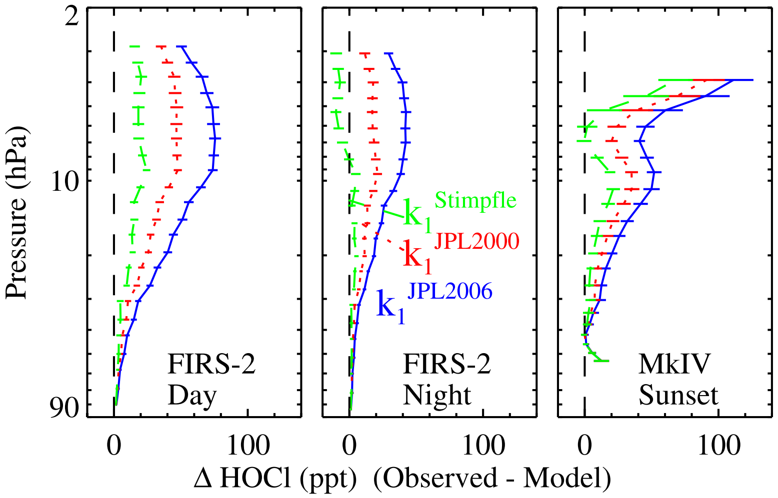

Figure 4. Difference between modeled and measured HOCl profiles, averaged over several mid-latitude flights. Model runs as in Figure 2. (left) Difference profiles for FIRS-2 daytime HOCl obtained on 29 September 1992, 22 May 1994, 19 September 2003, 23 September 2004, and 20 September 2005. (middle) The same for FIRS-2 nighttime HOCl. (right) Results for MkIV sunset profiles of HOCl obtained on 14 September 1992, 25 September 1993, 22 May 1994, 28 September 1996, 19 September 2003, 23 September 2004, and 20 September 2005.

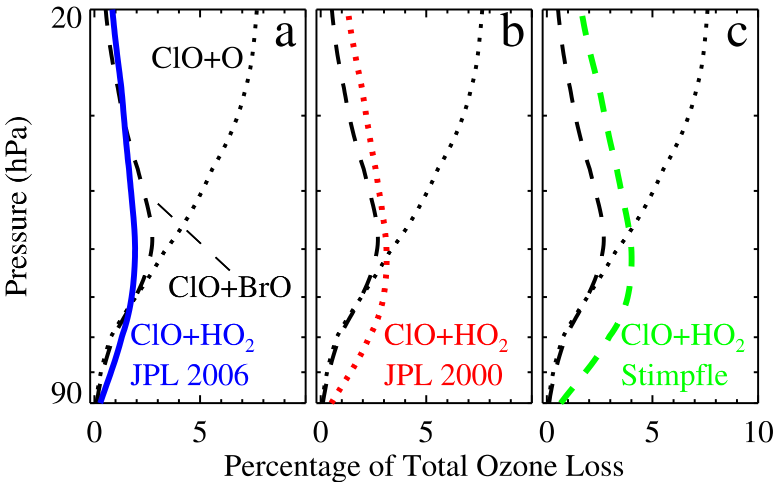

Figure 5. Calculated contribution of the three most important catalytic cycles involving ClO to 24-hour averaged ozone loss, for the 20 September 2005 flight, for model runs (a) $k_1^{JPL2006}$, (b) $k_1^{JPL2000}$, and (c) k_1^{Stimpfle}.

profiles (Figure 4, middle), and MkIV sunset profiles (Figure 4, right). The analysis clearly shows a large discrepancy between measured HOCl and model calculations using JPL 2006 kinetics. Notably, the discrepancy is present at day, night, and sunset, and is larger than the uncertainty in the HOCl loss terms. Model results using the *Stimpfle et al.* [1979] rate constant result in better agreement with observed HOCl for all viewing times.

[21] We have also run the photochemical model with the new *Hickson et al.* [2007] rate constant. The model HOCl profile obtained with this rate constant falls between model HOCl obtained with the JPL 2000 and JPL 2006 rate constants, and disagrees with measured HOCl within the range of uncertainty of the model.

[22] A recent satellite-borne MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) instrument has measured mid-day and night-time profiles of HOCl with global coverage [*von Clarmann et al.*, 2006]. They retrieved HOCl using HITRAN 2004, based on emission from the same HOCl lines measured by MkIV. They found general agreement with FIRS-2 profiles when trends in Cl_y were used to account for the difference in measurement dates. Thus the MIPAS data should also be consistent with a factor-of-two more HOCl than predicted by current models that use JPL 2006 kinetics.

6. Implications for Ozone Loss

[23] The discrepancies shown above suggest that present ozone assessment models may underestimate, by nearly a factor of two, the production rate of HOCl and hence the catalytic loss of ozone by the ClO + HO_2 cycle. However, an important caveat must be noted: ozone loss by ClO + HO_2 is important only in the lower stratosphere, whereas our ability to conduct meaningful comparisons of measured and modeled HOCl is restricted to the middle stratosphere. Care must be used in extrapolating results from the middle stratosphere to the lower stratosphere because of possible uncertainties in the p and T dependence of k_1. We believe our study highlights the need for further laboratory efforts to reduce the uncertainty of k_1 over the entire range of relevant conditions.

[24] Figure 5 shows the calculated contribution to ozone loss by the HOCl catalytic cycle compared with that for other catalytic cycles that involve ClO, for the three model runs. The factor-of-two discrepancy in rate constant translates into a similar range in calculated ozone loss by the HOCl cycle in the midlatitude lower stratosphere. Below ~21 km, ozone loss by this cycle is the most efficient loss process of all cycles involving ClO. This cycle dominates loss by the other cycles for the model run with $k_1^{Stimpfle}$, yet barely exceeds loss by the other cycles for the $k_1^{JPL2006}$ run. Therefore, the value of k_1 may have greatest impact on understanding trends in profiles of ozone in the lowermost stratosphere.

[25] **Acknowledgments.** Research at the Jet Propulsion Laboratory, California Institute of Technology, is performed under contract with the National Aeronautics and Space Administration (NASA).

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Text S1
Size: 7 KB
Format: TXT
Recommended viewer:
Caption: Description of the effect of the new HITRAN database on FIRS-2 and MkIV HOCl retrievals, and the effect of constraining the model to measured ClO and HO_2 on the model HOCl profile.

Figure S1
Size: 26 KB
Format: EPS
Recommended viewer: GhostView
Caption: Same as the first two panels in Figure 2 of the main text, with the addition of retrievals of HOCl found using the spectral linelist that preceded HITRAN 2004.

Figure S2
Size: 27 KB
Format: EPS
Recommended viewer: GhostView
Caption: FIRS-2 HOCl, the JPL 2006 model result, and the model result when constrained to measured ClO and HO_2, and the measured ClO and HO_2, respectively, for each instrument.

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Balloon-borne measurements of HOCl by MkIV (solar absorption in the mid-infrared) and by FIRS-2 (limb emission in the far-infrared) have been performed from the same platform for more than a decade. Until recently, the operational retrievals from the MkIV HOCl measurements had been based on the line list provided by HITRAN prior to 2004. FIRS-2 also had used the line list based on HITRAN prior to 2004; however, due to the limited coverage of the far-IR wavelength region in HITRAN, lines in that region were taken from the JPL submillimeter line catalogue [Pickett et al., 1998].

Using those databases, comparisons between the retrieved HOCl abundances from both instruments had shown significant inconsistencies, with values retrieved by MkIV having been about a factor of two lower than those retrieved by FIRS-2. Those old retrievals are shown in Figure S1 by the open symbols. While the old MkIV HOCl retrievals agree best with the model run using JPL 2006 kinetics, the old FIRS-2 HOCl retrievals agree best with the model run using a faster rate constant for HOCl formation, k1, the value obtained by Stimpfle et al. [1979]. This discrepancy has been discussed previously at various meetings (e.g., Kovalenko et al. [2004]).

The 2004 edition of HITRAN [Rothman et al., 2005] includes a major update of the HOCl spectroscopy. In the mid-infrared, positions and intensities were updated based on measurements by Vander Auwera et al. [2000], which led to a decrease in the mid-IR line intensities of about 60%. Far-infrared positions and intensities were adopted from measurements by Flaud et al. [1998]. We note that these values are very similar to the far-IR values that had been used previously to retrieve FIRS-2 HOCl.

Since the experiments by Vander Auwera et al. included simultaneous measurements in both the mid- and far-infrared, the line parameters in the mid- and far-infrared regions given by HITRAN should be internally consistent. In addition, air-broadened half-widths were adopted globally from the measurement of two lines by Shorter et al. [1997].

For the HOCl profiles presented in this paper, both MkIV and FIRS-2 retrievals use the HITRAN 2004 line list. For MkIV, the retrieved HOCl (closed square in panel b of Figure S1) increases by about 60% relative to a retrieval using HITRAN 2000. This increase is nearly equivalent to the decrease in line intensity because, at altitudes important for the study of HOCl, the vibrational transitions measured by MkIV are barely affected by collisions, and thus not sensitive to the change in air-broadened widths.

For FIRS-2, the use of HITRAN 2004 results in a change in HOCl abundance of only about 10% (closed circle in panel a of Figure S1) relative to retrievals we had conducted prior to the release of this new spectroscopic line list. Because the new HOCl far-IR line intensities in HITRAN 2004 are nearly the same as those in the line list used previously by FIRS-2, only the change in collisional broadening coefficient has an effect on the FIRS-2 retrieval. While the HOCl vibrational transitions measured by MkIV are not sensitive to collisions, the longer wavelength, HOCl rotational transitions measured by FIRS-2 are sensitive.

The use of the HITRAN 2004 line parameters has, for the first time, brought the mid-IR HOCl measurements of MkIV and the far-IR HOCl measurements of FIRS-2 into reasonable agreement, with both agreeing best with model runs using JPL 2006 kinetics and the value of k1 from Stimpfle et al. [1979].

To assess whether errors in the modeled profiles of ClO and HO2, precursors of HOCl, might be the cause of the discrepancy in modeled and measured HOCl, we examine how the HOCl profile would be affected if the model were constrained to measurements of these two precursors. We obtain a modified profile of HOCl by multiplying model HOCl by the ratio of measured-to-modeled precursor, for both precursors.

Figure S2 shows measured and modeled profiles of a) HOCl, b) ClO, and c) HO2. Measurements are shown by the symbols, model results using JPL 2002 kinetics by the solid blue line. Because several instruments have measured the precursor profiles, we have interpolated the measurements to a common vertical grid, the model altitude grid. The average of the measured precursor profiles is shown by the dotted blue lines in panels b) and c). We then multiply model HOCl (solid blue line in panel a) by the ratios of measured-to-modeled precursors. The resulting HOCl is shown by the dotted blue line in panel a.

It is seen that possible errors in the model estimate of the precursors ClO and HO2 are much too small to account for the discrepancy between modeled and measured HOCl.

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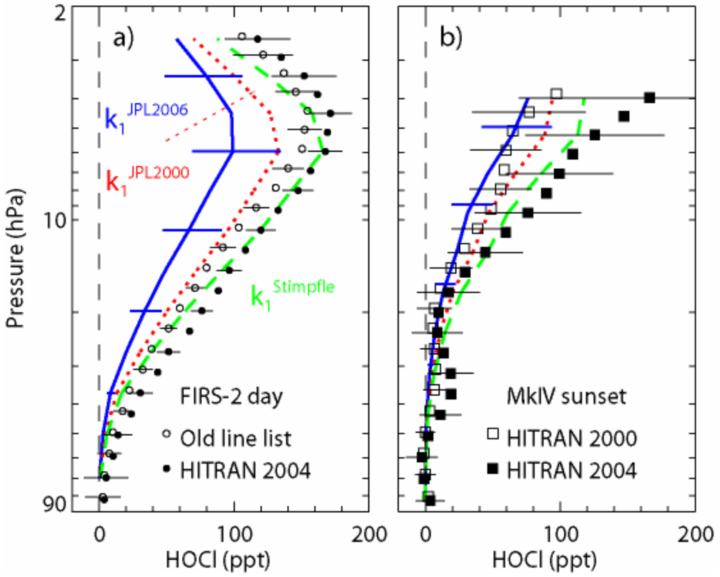

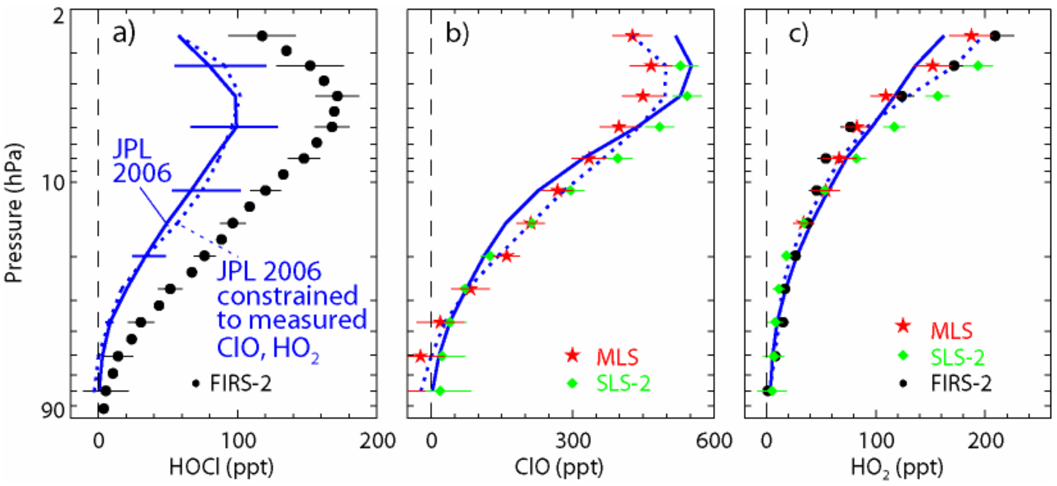
a)
b)
c)
Pressure (hPa)
2
10
90
HOCl (ppt)
0
100
200
ClO (ppt)
0
300
600
HO_2 (ppt)
0
100
200
JPL 2006
JPL 2006 constrained to measured ClO, HO_2
FIRS-2
MLS
SLS-2
MLS
SLS-2
FIRS-2