Observations of OH, HO_2, H_2O, and O_3 in the upper stratosphere: implications for HO_x photochemistry

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Abstract

Balloon-borne observations of concentrations of OH, HO_2, H_2O, and O_3 in the middle and upper stratosphere are used to test our understanding of HO_x photochemistry. Assuming our photochemical model is complete, the measured [OH] and [HO_2] above 38 km (where HO_x partitioning is no longer dependent on [NO]) are modeled best by calculations that use a 25% reduction in the ratio of the reaction rate constants for O+HO_2 and O+OH as well as either a 25% reduction of the rate constant of OH+HO_2 (the primary HO_x sink) or a 25% increase in HO_x production. All of these changes are consistent with the uncertainties in the recommended rate constants. The kinetic parameters required to explain our observations of [OH] and [HO_2] do not lead to a resolution of the long-standing "ozone deficit problem" above 45 km.

1. Introduction

HO_x (defined here as OH+HO_2) is produced in the upper stratosphere and mesosphere principally via

$$H_2O + O(^1D) \rightarrow OH + OH \quad (1)$$

and by photolysis of H_2O above 60 km. The primary HO_x loss reaction is

$$HO_2 + OH \rightarrow O_2 + H_2O, \quad (2)$$

although the reaction of OH with HNO_3 becomes an important HO_x sink in the lower and middle stratosphere. The partitioning between OH and HO_2 is driven mostly by the reactions

$$HO_2 + O \rightarrow OH + O_2, \quad (3)$$

$$OH + O \rightarrow O_2 + H, \quad (4)$$

$$HO_2 + NO \rightarrow OH + NO_2, \quad (5)$$

and

$$OH + O_3 \rightarrow HO_2 + O_2. \quad (6)$$

Reactions 3 and 4 dominate the partitioning of HO_x above approximately 38 km, while reactions 5 and 6 (along with HO_2+O_3) dominate at lower altitudes. The H atom produced in reaction 4 is quickly converted to HO_2 by reaction with O_2, which is about 10 times faster than its reaction with O_3 that recreates OH at these altitudes.

Recent measurements of [OH] and [HO_2] individually have suggested an incomplete understanding of HO_x chemistry in the middle atmosphere. *Summers et al.* [1997] reported measurements of [OH] between 50 and 80 km that were ∼25–30% lower than expected based on standard photochemical theory. *Sandor and Clancy* [1998] found that ground-based microwave measurements of [HO_2] were 25–30% higher than expected. Since neither of these studies obtained simultaneous measurements of [OH] and [HO_2], it is not possible to discern whether the reported discrepancies were due to errors in the partitioning of HO_x, in the balance of production and loss of HO_x, or a combination of both factors.

The Far Infrared Spectrometer (FIRS-2) simultaneous measurements of concentrations of OH, HO_2, H_2O, and O_3 presented here provide a stringent test of our understanding of the photochemistry of HO_x. We show: a) measured [OH] agrees reasonably well with, and measured [HO_2] is significantly higher than, values calculated using standard kinetic parameters for altitudes between 40 and 50 km; b) modifications to both the partitioning of HO_x and the balance of production and loss of HO_x are necessary to explain the observed [HO_2]/[OH] ratio and abundance of HO_x; c) the changes to reaction rates proposed by *Summers et al.* [1997] and *Sandor and Clancy* [1998] to explain their observations are inconsistent with the simultaneous FIRS-2 observations of [OH] and [HO_2]. Furthermore, the FIRS-2 observations are unlikely to help resolve the "ozone deficit problem" above 45 km. Models that describe well our observed profiles of [OH] and [HO_2] either have similar, or enhanced, imbalances between production and loss of O_3 compared to the standard calculation.

2. Measurements and Model

The FIRS-2 is a thermal emission far-infrared Fourier transform spectrometer developed at the Smithsonian Astrophysical Observatory and operates mostly from balloons [*Johnson et al.*, 1995]. The spectrometer has recently been upgraded with a new beamsplitter [*Dobrowolski and Traub*, 1996] to obtain nearly complete spectral coverage between 75 and 1000 cm^{-1} with high interferometric efficiency. Currently, FIRS-2 spectra yield vertical concentration profiles of over 28 molecules. Measured slant columns are fit in an onion-peeling fashion and a singular-value decomposition routine is then used to retrieve mixing ratios on a 1 km vertical grid [*Johnson et al.*, 1996]. The concentrations above the balloon altitude are determined from the observed overhead columns retrieved from the FIRS-2 spectra and constrained either by the profile shape calculated using the photochemical model described below or climatological profiles.

The measurements presented here were obtained during a balloon flight from Fairbanks, Alaska on 30 April 1997 as part of the ADvanced Earth Observing Satellite (ADEOS) Alaska validation campaign. We produced two sets of profiles: one from spectra obtained while observing to the north, at 9:15 ± 1 hr local solar time, centered at 69°N, 149°W and a second from spectra obtained while observing to the northwest, at 11:15 ± 1.5 hr local solar time, centered at 68°N, 157°W. The balloon float altitude was 37 km.

[OH] is retrieved from 11 rotational transitions between 83 and 230 cm^{-1} and [HO_2] is retrieved from 43 rotational transitions between 110 and 220 cm^{-1}. The systematic error due to uncertainties in the spectroscopic parameters for OH and HO_2 rotational transitions is small. Our estimate of the total systematic uncertainty for the retrievals presented here is 5% for [OH] and 3% for [HO_2].

Investigating HO_x photochemistry in the middle and upper stratosphere requires accurate measurements of [O_3] (used to derive concentrations of O and $O(^1D)$ as well as the photolytic environment) and [H_2O]. The FIRS-2 profiles of [O_3] are retrieved using rotational transitions between 80 and 130 cm^{-1} and ro-vibrational transitions between 750 and 810 cm^{-1}. The observed concentration profile of [O_3] is shown in Figure 1a, along with a profile obtained by an in situ UV photometer on the same gon-

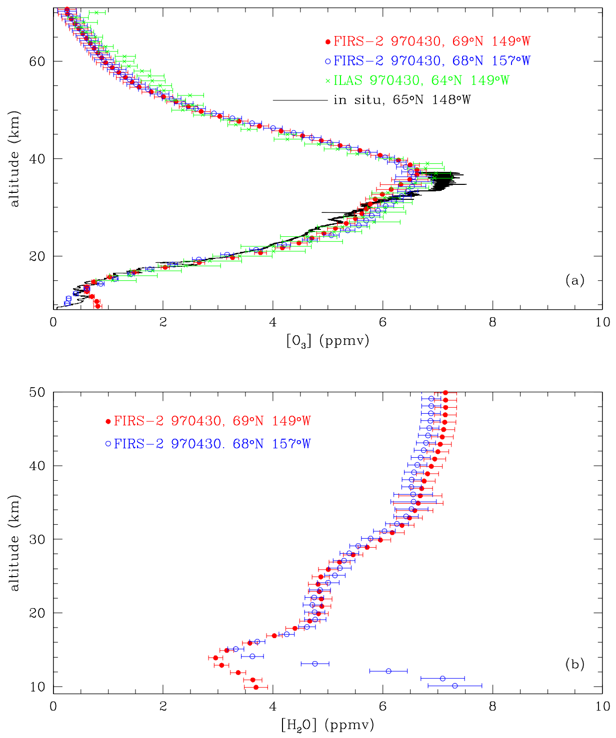

Figure 1. (a) Balloon-borne mixing ratios of O_3 retrieved by FIRS-2 and an in-situ photometer as well as ILAS during a nearly coincident occultation on 30 April 1997 in northern Alaska. (b) Mixing ratios of H_2O retrieved from the same FIRS-2 data set. FIRS-2 data points above 38 km are derived from column measurements constrained by climatological values. Measured O_3 and H_2O are used to constrain the photochemical model calculations.

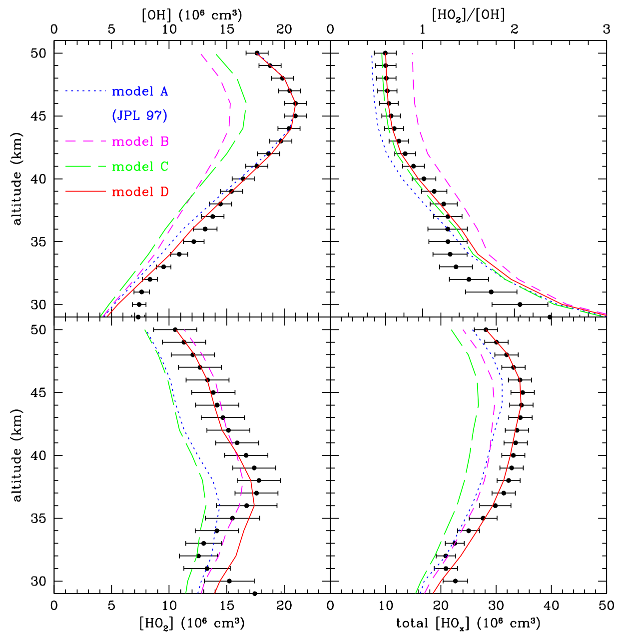

Figure 2. Measured and modeled concentrations of OH, HO_2, and HO_x as well as $[HO_2]/[OH]$ from the FIRS-2 balloon flight on 30 April 1997 for the first set of observations at 69°N, 149°W 9:15 local solar time. All model curves are constrained by simultaneous FIRS-2 measurements of temperature, O_3 and H_2O. Model A uses standard photochemical reaction rates and cross sections, model B has the rate constant for $O+HO_2$ decreased by 50%, model C has O+OH decreased by 20% and $OH+HO_2$ increased by 30%, and model D has the rate constants for $O+HO_2$ and $OH+HO_2$ both reduced by 25%.

dola and a nearby $[O_3]$ profile measured by the Improved Limb Atmospheric Sounder (ILAS) instrument (version 3.0 data) on board ADEOS. The good agreement between the FIRS-2, in-situ, and ILAS profiles (as yet unvalidated) below 38 km suggests ILAS has accurately measured $[O_3]$ in the middle stratosphere. Above 38 km, the overhead O_3 column retrieved by FIRS-2 is in good agreement with the column above 38 km determined from the ILAS profile. Thus, we are confident that the ILAS $[O_3]$ measurement is accurate (it a variation of about 10% depending on the inversion algorithm used) and confirms the climatological profile shape used to constrain the FIRS-2 profile above 38 km.

The FIRS-2 measurements of $[H_2O]$ are plotted in Figure 1b. $[H_2O]$ is retrieved using rotational transitions between 140 and 500 cm^{-1}, selected to reduce the systematic uncertainties to 5%. The profile shape above 38 km is constrained by climatology. The FIRS-2 concentrations of $[H_2O]$ above 35 km are ∼8% higher than those of HALOE for similar latitudes and time of year. Use of HALOE $[H_2O]$ would decrease the modeled HO_x discussed below by 4% and increase the difference between measured and calculated values.

The photochemical model employed here has been used previously to interpret data from aircraft, satellite, and balloon platforms [*Jucks et al.*, 1996 and references therein]. In the present analysis, the model is constrained by FIRS-2 measurements of $[O_3]$, $[H_2O]$, $[Cl_y]$, $[NO_y]$, $[N_2O]$ (to infer $[CH_4]$), and temperature in the middle and upper stratosphere.

3. Discussion

The measured concentration profiles of OH, HO_2, and total HO_x as well as $[HO_2]/[OH]$ between 30 and 50 km are shown in Figure 2. Only the first of the two sets of data is displayed here for simplicity, but both sets show quantitatively consistent comparisons with the model calculations discussed below. Above 35 km, measured concentrations of OH are in reasonable agreement with the values calculated using recommended reaction rates and absorption cross sections from *DeMore et al.* [1997] (model A) while measured concentrations of HO_2 are $\sim$25% higher than the calculated values from model A. The discrepancy for [HO_2] is similar to that reported by *Sandor and Clancy*, [1998] for altitudes above 50 km. The good agreement for [OH] is similar to that reported near 40 km by *Pickett and Peterson* [1996].

Summers et al. [1997] reported lower concentrations of OH between 50 and 80 km than calculated using recommended reaction rates and cross sections. They showed agreement with the MAHRSI observations of [OH] would be improved if either the rate constant of reaction 3 (k_3) were reduced by 50% (model B in Figure 2) or k_2 was increased by 20% and k_3 was reduced by 30% (model C in Figure 2). The latter changes are within the uncertainties given by *DeMore et al.* [1997]. Our models B and C use the same kinetic parameters as the similarly named models of *Summers et al.* [1997]. Model B is also similar to the kinetic change favored by *Sandor and Clancy* [1998] (they used a 40% reduction in k_3) to explain their measurements of [HO_2].

Neither model B or C lead to calculated profiles for both [OH] and [HO_2] that are consistent with the FIRS-2 observations. Both result in [OH] significantly lower than measured. The model C calculation also results in significantly lower [HO_2] than observed. The difference between the observed and modeled columns of OH and HO_2 between 38 and 50 km (using both sets of [HO_x] retrievals described above) has a reduced χ^2 of 5.3, 7.8, and 7.9 for models A, B, and C, respectively.

The contrasting conclusions regarding our understanding of HO_x photochemistry drawn from the FIRS-2 and MAHRSI observations appear to result from a fundamental measurement difference, since our model reproduces the *Summers et al.* [1997] calculations. The two measurements of [OH] are difficult to compare directly since 50 km is both the lowest altitude point reported by MAHRSI and the highest altitude point by FIRS-2. The differences between the concentrations of [OH] measured by MAHRSI and the model A calculations are close to the systematic uncertainties of 23% quoted in *Summers et al.* [1997].

The FIRS-2 observations of the [HO_2]/[OH] ratio imply the partitioning of HO_x is not calculated correctly using the kinetic parameters of *DeMore et al.* [1997]. This suggests either a modification to the ratio of k_3/k_4 is necessary (the observations cannot be used to discriminate between the two rates) or else there exists an undocumented reaction that converts OH to HO_2 that would need to proceed at an approximate 24 hour average rate of 2.8×10^5 molec/cm^3/sec at 48 km. Such a reaction is unlikely given the extensive laboratory studies of OH reactions over the past two decades. The measured [HO_2]/[OH] ratio is consistent with k_3/k_4 equal to 1.34 at 250 K. *Keyser* [1983] reported a laboratory measurement at room temperature for k_3/k_4 of 1.7 $\pm$ 0.2, with an overall experimental error of $\pm$25%. While the ratio of the rate constants for reactions (3) and (4) necessary to explain the FIRS-2 observations is systematically lower than the existing laboratory data, we note that the experiment of *Keyser* [1983] was conducted only at room temperature and that the ratio for k_3/k_4 required to account for the FIRS-2 observations is within the overall experimental error of the laboratory measurement.

The FIRS-2 observations of the abundance of OH and HO_2 imply also that the balance between production and loss of HO_x is not calculated correctly by the standard model. The reaction of OH and HO_2 [reaction (2)] is the dominant sink for HO_x in the upper stratosphere. Since the measured product of [OH]$\times$[HO_2] is larger than the product calculated using model A, either the production rate of HO_x must be increased or the rate constant of the loss reaction decreased to lead to better agreement with the measurements.

There are considerable uncertainties in the production rate of HO_x, which depends on the photolysis rate of O_3, the quantum yield of O(^{1}D), and k_1. The existing laboratory measurements of k_2 show wide variation, reflected in the large uncertainty (52% at 240 K) associated with the recommended rate [*DeMore et al.*, 1997]. Equivalent values for calculated [OH] and [HO_2] result if, instead of decreasing k_2, a comparable increase were used for k_1. Finally, we note that there is little coupling between the partitioning reactions and the production/loss reactions at these altitudes because the partitioning reactions occur at rates about 50 times the rate of the production/loss reactions. Consequently, changes alone in the rates of the production/loss reactions have little effect on the calculated [HO_2]/[OH] ratio.

Good agreement is obtained with the FIRS-2 observations of [OH] and [HO_2] above 35 km when the rate constants of reactions 2 and 3 are both reduced by 25% (model D in Figure 2). We emphasize that comparable results are obtained for $\sim$25% increases in the rates of reactions 1 and 4. The difference between the observations and model D profiles for [OH] and [HO_2] has a reduced χ^2 of 1.2; a 5% change in either rate alteration doubles the reduced χ^2. As with model C, the values of k_2 and k_3 adopted in model D are consistent with the uncertainties given by *DeMore et al.* [1997].

Below 35 km, reaction 5 starts to dominate HO_x partitioning. This is evident at the lower altitudes of the data presented in Figure 2, where the [HO_2]/[OH] ratio is small compared to the model, implying higher [NO] than calculated. Our simultaneous measurements of NO_2 and HNO_3 suggest that the model underestimates NO_x in a manner consistent with the imbalance in observed [HO_2]/[OH] (Jucks et al., manuscript in preparation).

4. Implications for Ozone

The required changes in rate constants needed to account for our observations of HO_x will have either a negligible or worsening effect on the "ozone deficit" problem above 45 km [*Osterman et al.*, 1997 and references therein]. Good agreement with the FIRS-2 measurements is obtained if the rate constant for $O+HO_2$ (k_3), the dominant rate limiting step for loss of odd oxygen above 45 km, is reduced by 25% together with either an increase in k_1 or a decrease in k_2 (model D). Since observed [HO_2] is roughly 25% higher than values calculated using standard kinetics (model A), the calculated imbalance between production and loss of odd oxygen found using model D (loss is 30% greater than production at 48 km) is nearly identical to that found using model A. If the rate of O+OH (k_4) is instead increased by 25% a larger imbalance between production and loss of odd oxygen results (loss $\sim$50% greater than production at 48 km) because the higher than expected concentrations of [HO_2] are no longer offset by a change in the rate of the limiting step. *Sandor and Clancy* [1998] proposed that reducing k_2 by 40% would resolve the ozone deficit above 45 km. However, as noted above, this change alone results in discrepancies between theory and FIRS-2 observations of [OH], and consequently we do not consider it to be a viable solution to the ozone deficit problem.

It appears that the solution to the"ozone deficit" problem at these altitudes lies either with the calculated production rate of odd oxygen or with calculated concentrations of O. There are no observational constraints on the calculated concentrations of O at the required quantitative level. Recent studies have proposed scenarios involving vibrationally excited O_2 that could lead to increased production of odd oxygen, but critical aspects of this process involving the quenching of O_2 (v>26) await laboratory confirmation [*Toumi et al.*, 1996]. This scenario would have the largest effect on calculated production rates near 48 km, and have a significantly lesser effect near 35 km, where calculated production and loss are found to balance.

Acknowledgments We are grateful to the Japanese Space Agency (NASDA) for funding the balloon flight on 30 April 1997 from Fairbanks, Alaska as part of the Alaska Balloon Campaign correlative measurement program of the ADEOS satellite and to NASA's Upper Atmosphere Research program for support of work at SAO (grant NSG–5175) and JPL. We thank George Dobrowolski and George Laframboise of the National Research Council, Canada for their significant contribution to the development of the new beamsplitter used to obtain the data presented here. We appreciate the useful suggestions to the manuscript provided by Paul Wennberg. We are grateful to the Jet Propulsion Laboratory Atmospheric Ballooning group for gondola support and to the National Scientific Balloon Facility for launch services.

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