

Twilight observations suggest unknown sources of HO_x

P.O. Wennberg¹, R.J. Salawitch², D.J. Donaldson³, T.F. Hanisco⁴, E.J. Lanzendorf⁴, K.K. Perkins⁴, S.A. Lloyd⁵, V. Vaida⁶, R.S. Gao⁷, E.J. Hints⁴, R.C. Cohen⁸, W.H. Swartz⁵, T.L. Kusterer⁵, D.E. Anderson⁵.

Abstract. Measurements of the concentrations of OH and HO₂ (HO_x) in the high-latitude lower stratosphere imply the existence of unknown photolytic sources of HO_x. The strength of the additional HO_x source required to match the observations depends only weakly on solar zenith angle (SZA) for 80° < SZA < 93°. The wavelengths responsible for producing this HO_x must be longer than 650 nm because the flux at shorter wavelengths is significantly attenuated at high SZA by scattering and absorption. Provided that the sources involve only a single photon, the strength of the bonds being broken must be < 45 kcal mole⁻¹. We speculate that peroxyacetic acid (HNO₄) dissociates after excitation to an unknown excited state with an integrated band cross section of 2–3 × 10⁻²⁰ cm² molecule⁻¹ nm (650 < λ < 1250 nm).

Introduction

Measurement of the SZA dependence of short-lived radical species such as OH and HO₂ provides insight into their sources [e.g. Salawitch *et al.*, 1994]. In this letter we report twilight observations from a NASA ER-2 aircraft obtained near Fairbanks, Alaska during the 1997 Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) campaign. Observations at high latitudes are exceptionally well suited to this analysis: because of the slowly varying SZA, [HO_x] remains near instantaneous steady state ($P_{HO_x} \approx L_{HO_x} \gg d[HO_x]/dt$) at SZA as large as 93°.

Previously, high-SZA measurements of HO_x were made during the 1993 Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE). These observations showed that [HO_x] was higher than expected and implied the existence of unknown sources of these radicals present throughout the day. Most pronounced was the rapid onset of [HO₂] in the early morning – consistent with nighttime production of a photo-labile hydroxyl-containing species. Some of us speculated that HNO₄ might be hydrolyzed on sulfate aerosols producing HONO [Salawitch *et al.*, 1994]. Subsequent studies showed, however, that such hydrolysis does not occur [Zhang *et al.*, 1997]. After the SPADE observations, Hanson and Ravishankara [1995] discovered that BrONO₂ was hydrolyzed to HOBr in sulfuric acid. This production of HOBr

together with the recently discovered transition to a low-lying triplet state of HOBr centered near 500 nm [Barnes *et al.*, 1996] leads to significant production of HO_x at sunrise in model calculations [e.g. Lary *et al.*, 1996].

Recent studies have pointed to other processes that produce HO_x near twilight. Studies of the photolysis of O₃ have shown that O(¹D) is produced in a spin-forbidden process at wavelengths as long as 411 nm, significantly increasing the production rate of O(¹D) for SZA > 85° [Ravishankara *et al.*, 1998 and references therein]. Recently, Donaldson *et al.* [1997] have suggested that excitation of vibrational overtones of the OH stretch in HNO₃ and HNO₄ may provide a significant source of HO_x at high SZA.

HO_x at High SZA During POLARIS

The high-latitude, high-SZA observations obtained during POLARIS are distinct from those of SPADE and provide a different test of HO_x photochemistry. Nighttime is shorter; the lower stratosphere is warmer (228 vs. 212 K); total reactive nitrogen (NO_y) is a factor of two higher; and [NO₂] is nearly five times larger. In the intervening four years, aerosol surface area has declined by more than a factor of five.

In this study we compute the diurnal variation of [OH] and [HO₂] using a model constrained with measured values of pressure, temperature, aerosol surface area, and the concentrations of radical precursors (e.g. O₃, H₂O, and CH₄) (Table 1). Inorganic bromine, Br_y, and chlorine, Cl_y, are inferred from measurements of their source gases made by the whole air sampler and the airborne gas chromatograph. The O₃ column and its altitude distribution are inferred from Total Ozone Mapping Spectrometer (TOMS) data and from O₃ measurements obtained on the ER-2 and balloon-borne sondes. At SZA < 85°, this technique agrees with overhead O₃ measured by the ER-2 UV/Vis spectrometer. For SZA > 85°, however, the overhead O₃ column inferred from the spectrometer is not considered reliable [C.T. McElroy, personal communication]. TOMS reflectivity measurements are used to constrain the albedo along the flight track.

Interpretation of the HO_x observations requires correct representation of NO_x in the model because numerous processes couple these radicals. For most of the POLARIS observations of [NO] and [NO₂] are 20 – 40% larger than calculated using rate coefficients from DeMore *et al.* [1997] (Gao *et al.* [1999]; Osterman *et al.* [1999]). To assure calculated NO_x at twilight matches observation, we use recently reported rate coefficients for the reactions of OH with HNO₃ and NO₂ [Brown *et al.*, 1999; Dransfield *et al.*, 1999] and account for the remaining model-measurement disagreement (<10%) by relaxing the requirement that the partitioning between NO_x and NO_y be in steady-state.

Figure 1 shows the measured [HO₂] on 30 April and 9 May 1997. For these flights, the pilot flew a 'race-track' pattern

¹California Institute of Technology, Pasadena.

²Jet Propulsion Laboratory, California Inst. of Tech., Pasadena.

³Department of Chemistry, University of Toronto, Canada.

⁴Department of Chemistry, Harvard University, Cambridge, MA.

⁵Applied Physics Lab., Johns Hopkins Univ., Laurel, MD.

⁶Department of Chemistry, University of Colorado, Boulder.

⁷NOAA Aeronomy Laboratory, Boulder, CO.

⁸Department of Chemistry, University of California, Berkeley.

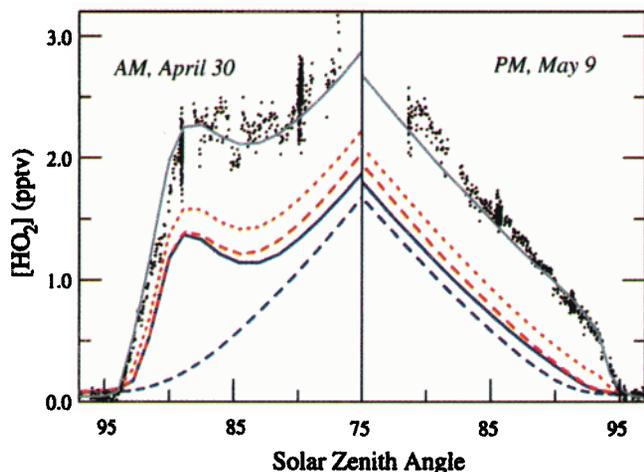


Figure 1. Measurements and model calculations for $[\text{HO}_2]$ on 30 April 1997 and 9 May 1997. All calculations use recently reported rate coefficients for the reactions of OH with NO_2 and HNO_3 . The solid blue line depicts a calculation using rate coefficients and cross sections from DeMore *et al.* [1997] for all other processes (JPL97*). The blue dashed line shows the same calculation without allowing for the hydrolysis of BrONO_2 . The red dashed line is JPL97* with the addition of the spin-forbidden production of $\text{O}(^1\text{D})$ in the near UV. The red dotted line displays a calculation that adds, in addition, production of HO_x from the excitation of overtones of the OH stretch in HNO_3 and HNO_4 . The gray solid line is a model that includes an additional photolytic pathway for HNO_4 placed at 800 nm (see text for details).

for nearly seven hours. Minimal variation ($\pm 15\%$) in the mixing ratio of long-lived tracers such as O_3 , CH_4 , N_2O , and NO_y was observed at $75^\circ < \text{SZA} < 97^\circ$. The solid blue line displays a calculation using, with the exception of the reactions noted above, rate coefficients and absorption cross sections from DeMore *et al.* [1997]. The observed $[\text{HO}_2]$ is larger than calculated by essentially a constant 0.75 pptv.

Potential systematic errors in the HO_x observations may be as large as 30% with an additional zero offset of ± 0.05 pptv. The precision of the calibration of the instrument, however, is much better: any systematic error will not change significantly from flight to flight or vary with SZA. This precision is critical to this analysis; although differences between the observations and calculated $[\text{HO}_x]$ at low SZA are not significant, the fractional variation of the difference with SZA is significant. At 92° SZA, this difference is greater than 60%. The comparison for OH is essentially the same, though the signal-to-noise ratio of the OH observations is lower because its concentration is ten to fifteen times smaller.

Errors in the representation of bromine chemistry cannot account for all the differences shown in Figure 1. The heterogeneous reaction of BrONO_2 with H_2O is calculated to convert more than 60% of the Br_y to HOBr over night, leading to a rapid increase in calculated $[\text{HO}_x]$ in the early morning. The blue dashed line (Figure 1) shows a calculation without this hydrolysis reaction. We use a reaction probability (γ) of 0.8. By assuming $\gamma = 1$ and increasing our estimate for Br_y by $\sim 30\%$, the agreement with measured $[\text{HO}_2]$ at sunrise is significantly improved. These changes however, do not improve agreement at sunset. Furthermore, recent laboratory data sug-

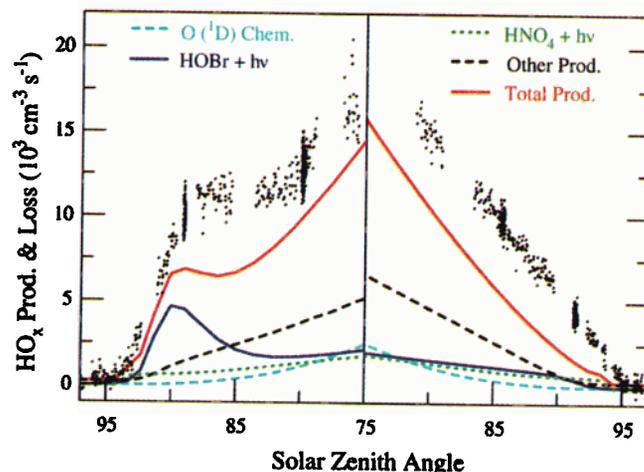


Figure 2. Production and loss rate of HO_x . In the full model (dotted red Figure 1), HO_x production from $\text{O}(^1\text{D})$ chemistry is important only at the lowest SZA. At high SZA, production is dominated by photolysis of HO_x reservoirs such as HNO_3 , HNO_4 , and HOBr. Photolysis of HOCl and methane oxidation make up most of the undifferentiated sources. The HO_x loss rate (data points) is determined from the measured abundances of HO_x , NO_x , and NO_y ($[\text{HNO}_3]$ is estimated by $[\text{NO}_y] - [\text{NO}_x] - [\text{ClNO}_3] - 2 \times [\text{N}_2\text{O}_5]$, where $[\text{N}_2\text{O}_5]$ is estimated from measured NO_x). The HO_x sink exceeds the calculated source by nearly a constant amount for $\text{SZA} \leq 93^\circ$.

gest that γ is likely 2–4 times smaller at $T = 230$ K [D. Hanson, personal communication].

Including the spin-forbidden production of $\text{O}(^1\text{D})$ in the photolysis of O_3 (Figure 1) has a negligible effect on $[\text{HO}_2]$ at high SZA because production of HO_x is dominated by processes involving reservoir species such as HNO_3 , HNO_4 , and

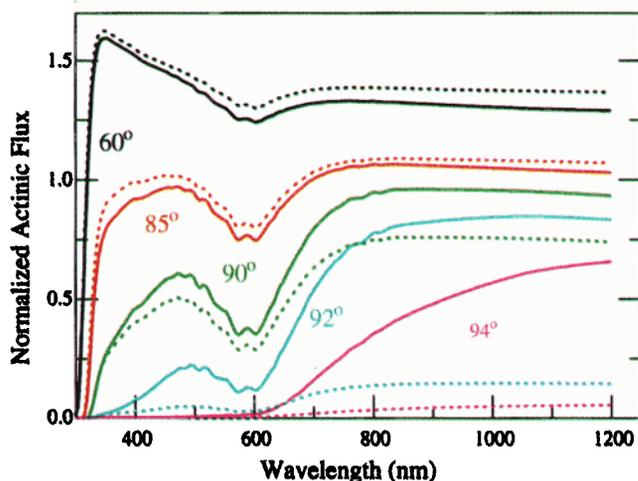


Figure 3. The local actinic flux at 20 km divided by the flux at the top of the atmosphere (F/F_0) depends strongly on SZA for wavelengths < 650 nm in the POLARIS atmosphere (solid lines). With heavy aerosol loading during the 1993 SPADE campaign (defined in Salawitch *et al.* [1994]), F/F_0 (dashed lines) was much lower at high SZA. Aerosol optical depth is determined from remote observations by the SAGE II instrument.

Table 1. Model Constraints

	30 April 1997	9 May 1997
Temperature	228 K	228 K
Pressure	66.0 mb	62.5 mb
Latitude	64.0°N	64.3°N
H ₂ O / CH ₄	4.8/1.3 ppmv	4.8/1.3 ppmv
O ₃	2.4 ppmv	2.6 ppmv
CO	12.5 ppbv	12.5 ppbv
NO _y	7.5 ppbv	7.5 ppbv
Br _y /Cl _y	12.9/1780 pptv	12.9/1780 pptv
NO _x at solar noon	1.0 ppbv	1.05 ppbv
O ₃ column (above ER-2)	203 DU	201 DU
O ₃ column (Total)	380 DU	390 DU
Albedo	0.25	0.10
Aerosol surface area	1 μm ² cm ⁻³	1 μm ² cm ⁻³

HOBr rather than by O(¹D) chemistry (Figure 2). For example, the minor HO_x source from thermal decomposition of HNO₄ is calculated to exceed production from O(¹D) chemistry by a factor of five at SZA = 90°, even when the spin forbidden process is included. We have assumed an O(¹D) quantum yield of 0.06 for 329 < λ < 411 nm.

The red dotted line in Figure 1 displays a calculation that includes the dissociation of HNO₃ and HNO₄ by photoexcitation of overtones of the OH vibrational stretch. The HNO₃ overtone intensities used here are from Donaldson *et al.* [1998]. Excitation of the OH stretch (ν₁) in HNO₃ to 5ν₁ (5 quanta) is partially dissociative and we use the quantum yield from Donaldson *et al.* [1997]. Only 3 quanta of excitation of the OH stretch are required to exceed the N-OOH bond strength in HNO₄ (D₀=22.8 kcal mole⁻¹ [Zabel, 1995]). The gas-phase cross sections for this transition are unknown. We use measurements of the HNO₄ cross sections obtained in a solution of concentrated H₂SO₄ prepared by reacting NaNO₂ with H₂O₂ (a modification of the procedure of Appelmann and Gosztola [1995]) [Donaldson *et al.*, in preparation]. The integrated intensity of 3ν₁ for HNO₄ was 1.3 ± 0.5 times 3ν₁ for HNO₃ determined in the same fashion. We assume that the gas phase intensities scale similarly. Note that the HO_x observations cannot be used to distinguish between sources of OH and HO₂ because these species are interconverted on a time scale of less than 1 min. The increase in calculated [HO₂] between the red dashed and dotted lines is entirely due to the different photolysis rate of HNO₄. Although included, the increase in the photolysis rate of HNO₃ neither significantly enhances [HO_x] nor alters the partitioning of NO_y.

Figure 2 illustrates the diurnal dependence of HO_x sources in the full model and the strength of the HO_x sink determined from the atmospheric observations and the relevant rate coefficients. The calculated source and sink differ by essentially a constant amount for SZA ≤ 93° and therefore the 'missing' source strength depends only weakly on SZA during daylight. The imbalance between production and loss of HO_x cannot be attributed to an excess sink because the observations imply that the imbalance is independent of [HO_x].

In Figure 3, the calculated actinic flux normalized to the flux incident on the Earth's atmosphere (F/F₀) is shown as both a function of SZA and wavelength. Two radiative transfer programs were examined for this study [Salawitch *et al.*, 1994; Anderson *et al.*, 1995] and produce essentially identical results provided that the same ozone profiles are used (differ-

ences <10%, for F/F₀ > 1 × 10⁻⁸). For SZA ≥ 92°, significant values of F/F₀ occur only for wavelengths > 650 nm (the end of the O₃ Chappius band). Comparison of the SZA dependence of the missing source and radiation field suggests that the photolysis must occur in the red / near-IR region of the spectrum. The calculations shown in Figure 3 include the effects of refraction and aerosol scattering, but do not include the narrow absorption features in the visible / near IR due to O₂, H₂O, and O₂ collision pairs. For the aerosol loading characteristic of the POLARIS atmosphere, the effects of aerosol scattering and refraction are equal but of opposite sign. Uncertainty in the radiation field for SZA > 93° is large due to clouds. We have assumed (based on TOMS climatology) that clouds are present at 500 mb. Such clouds advance sunset and delay sunrise by nearly 1°.

Could excited-state O₂ chemistry be the missing source? Toumi [1993] has suggested that O₂(b¹Σ_g⁻) + H₂ would be an important HO_x source even if only a small fraction of the total rate of this reaction produced OH. Even though O₂(b¹Σ_g⁻) is produced in the near IR, this process cannot be responsible for the HO_x production at high SZA because the large optical depth at the O₂ A,B, and γ bands leads to a strong SZA dependence for the production rate of O₂(b¹Σ_g⁻). (P_{SZA=75} > 10 × P_{SZA=92}, [M. Mlynchak and B.T. Marshall, pers. comm.]). For the conditions described in Table 1 this source cannot be important at twilight and would only be important for midday [HO_x] if the quantum yield for HO_x production is ~200%.

In contrast to the observations obtained during POLARIS, the 1993 SPADE measurements do not suggest significant production of HO_x at SZA > 90° [Salawitch *et al.*, 1994]. We find that the diurnal dependence of [HO_x] measured during SPADE is, within the uncertainty of the measurements, adequately described by the full model (*e.g.* red dotted model, Figure 1). However, the SPADE observations are not inconsistent with the POLARIS measurements because in 1993 the stratospheric aerosol loading was sufficiently high that aerosol scattering significantly darkened the sky at SZA ≥ 91° throughout the visible / near IR (Figure 3).

Missing photochemistry of HNO₄?

The requirement that the missing HO_x sources be produced by solar radiation at λ > 650 nm places a significant constraint on the energetics of these processes. The thermodynamic limits for the production of HO_x from HOCl, H₂O₂, HONO, HOBr, HNO₃, and HNO₄ are 518, 557, 572, 591, 598, and 1250 nm, respectively. Thus, HNO₄ is one of the few HO_x reservoir species that has a sufficiently weak bond to allow photodissociation with single photons of these energies (650 nm photons have an energy of 44 kcal mole⁻¹).

As illustrated in Figure 1, the HO_x chemistry at high SZA can be balanced by the addition of a photolytic pathway for HNO₄ with a photolysis rate coefficient of 1 × 10⁻⁵ s⁻¹ (at F/F₀ = 1) arbitrarily placed at 800 nm. Including this process in the model increases the 24 hour average [HO_x] by ~20-30% in these airmasses and improves the agreement between measured and calculated HO_x for all POLARIS flights. This process would also resolve the model-measurement discrepancies for [HNO₄] obtained by the MkIV balloon-borne interferometer during POLARIS [Salawitch *et al.*, in prep.]. With this process included, the calculated [HNO₄] drops by a factor of ~2, reconciling the calculations with observations.

This result is largely insensitive to assumptions about the UV cross sections of HNO₄. The two studies used in the JPL evaluation differ significantly at $\lambda > 310$ nm [Molina and Molina, 1981; Singer *et al.*, 1989] and the DeMore *et al.* [1997] recommendation does not extend beyond 325 nm. We have assumed that the UV cross section for HNO₄ are 0 for $\lambda > 325$ nm. We have performed sensitivity studies to this assumption and find that our conclusion about the need for an additional HO_x source longward of 650 nm is not changed. Although larger UV cross sections for HNO₄ improve the agreement for [HO_x] at low SZA, the agreement at SZA $> 90^\circ$ is not sensitive to these cross sections because the actinic flux at $\lambda < 400$ nm is negligible at these SZA. The same is true for uncertainty in the ozone profile; a smaller ozone column above the ER-2 improves agreement at low SZA but does not change the model result at high SZA.

What spectroscopic transition could produce this photolysis? The 3v₁ overtone of HNO₄ is five times too weak. It is possible that combination bands of 2v₁ may be involved. These transitions have not been observed, however, and the thermochemistry of HNO₄ is sufficiently uncertain that it is unclear whether excitation of these modes would be dissociative. Perhaps a singlet-triplet transition exists in HNO₄ as has been shown to occur in HOBr [Barnes *et al.*, 1996]. Photolysis of HNO₄ in a transparent region of the red / near-IR with an integrated band cross section of only 2.5×10^{-20} cm² molecule⁻¹ nm matches the required source of HO_x (Figure 1). This increased photolysis rate would reduce the calculated importance of HNO₄ both as a NO_x reservoir and a HO_x sink. Work is underway at Caltech to study the photodissociation of HNO₄ in the red / near-IR.

Conclusion

High-SZA observations of HO_x have demonstrated that a source of HO_x $\approx 3 \times 10^3$ molecules cm⁻³ s⁻¹ persisting to very high SZA is missing from the photochemical description of the stratosphere. The source likely involves photolysis in the red or near IR because the optical depth of the atmosphere at shorter wavelengths is large at high SZA. Until the source molecules are identified, however, we cannot determine the extent to which these processes are important globally.

Acknowledgements. We thank NASA's Upper Atmosphere Research and the Atmospheric Effects of Aviation Programs for supporting the POLARIS field campaign (M. Kurylo, P. DeCola, and R. Kawa, project managers). POW acknowledges additional support from the NSF (ACM-9612282) for this work. DJD acknowledges NSERC for partial support of this work. VV acknowledges NSF for support. We thank C. Webster (for CH₄ and CO), R. May (for H₂O), J. Margitan and M. Proffitt (for O₃), C. Wilson and C. Brock (for aerosol surface area), J. Elkins and E. Atlas (for organic halogens), L. Thomason (for aerosol extinction), R. McPeters (O₃ column and reflectivity), and M. Mlynchak and B.T. Marshall (for O₂(b¹Σ_g)). We appreciate the leadership of D. Fahey and P. Newman, POLARIS lead scientists. We thank A. Tuck for motivating this study. A portion of this work was performed at JPL under contract from NASA.

References

- Appelman, E.H. and D.J. Gosztola, Aqueous peroxyntic acid (HOONO₂) - A novel synthesis and some chemical and spectroscopic properties, *Inorg. Chem.*, **34**, 787-791, 1995.
- Anderson, D.E., *et al.*, Impact of aerosols and clouds on the troposphere and stratosphere radiation-field with application to twilight at 20 km. *J. Geophys. Res.*, **100**, 7135-7145, 1995.
- Barnes, R.J., *et al.*, Observation of a new absorption band of HOBr and its atmos. implications, *J. Phys. Chem.*, **100**, 453-457, 1996.
- Brown, S.S., *et al.*, Reconsideration of the rate constant for the reaction of OH with HNO₃, *J. Phys. Chem.*, in press, 1999.
- Donaldson, D.J., *et al.*, Atmospheric radical production by excitation of vibrational overtones via absorption of visible light, *Geophys. Res. Lett.*, **24**, 2651-2654, 1997.
- Donaldson, D.J., *et al.*, Absolute intensities of nitric acid overtones, *J. Phys. Chem. A*, **102**, 5171-5174, 1998.
- Dransfield, T.J., *et al.*, Temperature and pressure dependent kinetics of OH with NO₂, *Geophys. Res. Lett.*, **26**, 687-690, 1999.
- Gao, R.S., *et al.*, A comparison of observations and model simulations of the NO_x/NO_y ratio in the lower stratosphere, *Geophys. Res. Lett.*, **26**, 1153-1156, 1999.
- Hanson, D.R., Ravishankara, A.R. Heterogeneous chemistry of bromine species in H₂SO₄, *Geophys. Res. Lett.*, **22**, 385-388, 1995.
- Lary, D.J., *et al.*, Heterogeneous atmospheric bromine chemistry, *J. Geophys. Res.*, **101**, 1489-1504, 1996.
- Molina, M.J. and L.T. Molina, UV absorption cross sections of HO₂NO₂ vapor, *J. Photochem.*, **15**, 97-108, 1981.
- Osterman, G.B., *et al.*, The partitioning of NO_y species in the summer Arctic stratosphere, *Geophys. Res. Lett.*, **26**, 1157-1160, 1999.
- Ravishankara, A.R., *et al.*, Photochemistry of ozone: Surprises and recent lessons, *Science*, **280**, 60-61, 1998.
- Salawitch, R.J., *et al.*, The diurnal variation of hydrogen, nitrogen, and chlorine radicals: Implications for the heterogeneous production of HNO₂, *Geophys. Res. Lett.*, **21**, 2551-2554, 1994.
- Singer, R.J., *et al.*, Measurement of the absorption cross-section of peroxyntic acid between 210 and 330 nm in the range 253-298 K, *J. Photochem. Photobiol. A*, **48**, 17-32, 1989.
- Toumi, R., A potential new source of OH and odd-nitrogen in the atmosphere, *Geophys. Res. Lett.*, **20**, 25-28, 1993.
- Zabel, F., Unimolecular decomposition of peroxyntates, *Zeitschrift für Physikalische Chemie*, **188**, 119-142, 1995.
- Zhang, R., M.T. Leu, L.F. Keyser, Heterogeneous chemistry of HO₂NO₂ in H₂SO₄ (l), *J. Phys. Chem. A*, **101**, 3324-3330, 1997.
- P. Wennberg, MS 150-21, Caltech, 1200 E. California Blvd., Pasadena, CA 91125, (wennberg@gps.caltech.edu).
- R. Salawitch, JPL, 4800 Oak Grove Dr., Pasadena, CA 91109.
- T. Hanisco, E. Lanzendorf, E. Hintsa, K. Perkins, Department of Chemistry, Harvard, 12 Oxford St., Cambridge, MA 02138.
- D. Donaldson, Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1.
- V. Vaida, Department of Chemistry, Univ. of Colorado, Boulder, CO, 80309.
- S. Lloyd, W. Swartz, T. Kusterer, D. Anderson, APL, The Johns Hopkins University, Johns Hopkins Road, Laurel, Maryland 20723.
- R.S. Gao, NOAA Aeronomy Laboratory, Boulder, CO, 80307.
- R. Cohen, University of California, Berkeley, CA 94720.

(Received December 21, 1998; revised March 12; accepted March 24, 1999.)