[illegible]

[illegible] / IN / 25

"Laboratory Studies of the Photochemistry of Peroxynitric Acid"
Final Report, July 2nd, 2002.
Paul O. Wennberg, P.I.
January 1, 2000-March 31, 2002
California Institute of Technology
1200 California Boulevard
Pasadena, CA 91125
NASA Goddard - Grant NAG5-9307

Observations of odd hydrogen radicals at high SZA in the lower stratosphere have demonstrated that our understanding of the HO_x chemistry is incomplete [Wennberg *et al.*, 1994a; Salawitch *et al.*, 1994; Wennberg *et al.*, 1999]. In particular, the concentrations of the HO_x radicals are significantly larger than expected under weak photolytic conditions. Donaldson *et al.* [1997] have speculated that excitation of overtones of the OH stretching frequency in molecules such as HNO_3 and HO_2NO_2 may be significant sources of HO_x under these conditions. Although weak, vibrationally mediated photolysis may be important because it occurs in the near IR and visible and can provide energy in excess of the dissociation energy (D_o):

$$HONO_2 + h\nu \rightarrow OH + NO_2 \ (D_o \sim 600 \text{ nm})$$

and

$$HOONO_2 + h\nu \rightarrow OH + NO_3 \ (D_o \sim 735 \text{ nm})$$

$$HOONO_2 + h\nu \rightarrow HO_2 + NO_2 \ (D_o \sim 1250 \text{ nm})$$

In this project we developed instrumentation to characterize the photodissociation yields of hydroxyl containing compounds in the visible and near IR. This effort has involved coupling a tunable photolysis optical parametric oscillator (OPO) laser system with precise determination of the hydroxyl radical. The OPO system [Wu *et al.*, 1997] was developed with support from the NSF Major Research Instrumentation Fund in a proposal entitled "Development of Novel, Compact Light Sources for Advanced Spectroscopy in Atmospheric Science and Materials Research" (Geoffrey A. Blake, P.I. California Institute of Technology). The preliminary study of HO_2NO_2 forms the basis for a Ph.D. thesis recently defended by Dr. Hui Zhang. This major findings of this study have been published recently (Roehl *et al.*, *2002*, Salawitch *et al.*, *2002*).

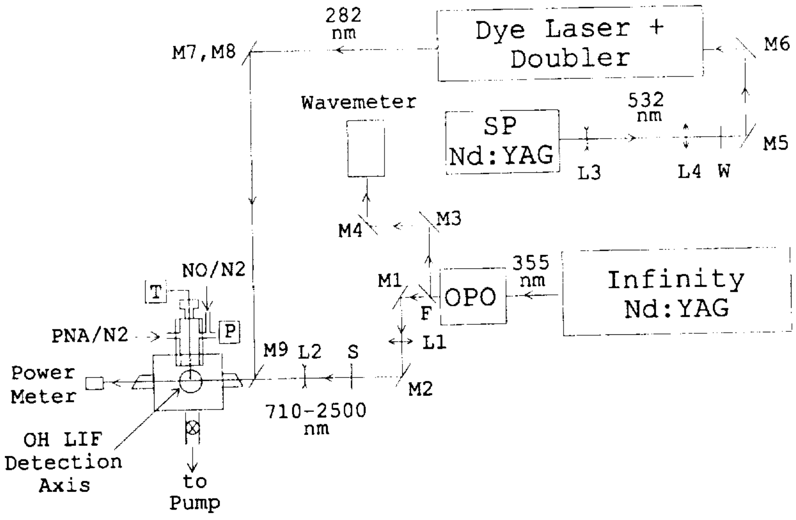

Figure 1. The HO_x action spectrum apparatus.

Figure 1 illustrates the basic architecture of the apparatus. A jacketed glass flow tube is used to introduce the HO_2NO_2 (PNA) into the photolysis region. Temperature control is maintained by circulation of chilled water (273 K) in the outer jacket. The N_2 carrier gas (~ 200 sccm at 3-25 torr total pressure) is mixed with NO (2000 ppmv NO in N_2, Matheson) to produce a NO density in the flow tube of approximately 3×10^{14} molecules cm^{-3}. This density is sufficient to insure that HO_2 produced in the photolysis beam is converted to OH in a fraction of a millisecond. With the NO turned off, the chemistry can be tested for OH production.

HO_2NO_2 is prepared in a nitrogen-purged glove box according to the method described by Kenley *et al.* [1981]. Briefly, ~1 g BF_4NO_2 is slowly added into 95+ wt% H_2O_2. The mixture is stirred in a jacketed glass vessel with water, cooled to ~273K, circulating around it. Once the synthesis is complete, the mixture is transferred to a glass bubbler and the assembly is immersed into an ice water bath. This synthesis produces HO_2NO_2 with some impurities. Nitric acid is present in the initial boil-off but after a few minutes is nearly gone. H_2O_2 is the major impurity and comprises as much as 50% of the HO_2NO_2 produced by this source at the end of each experiment. Typically, $1 - 5 \times 10^{14}$ molecules cm^{-3} of HO_2NO_2 is used in the flow tube.

The photolysis source is an OPO pumped by a high power pulsed Nd:YAG laser frequency tripled to 355 nm (Coherent). At a pulse repetition frequency of 100 Hz, 200 - 400 mW of radiation is produced in the idler beam at wavelengths between 800 and 2000 nm. The visible OPO signal beam is separated (F) and directed to a Burleigh pulsed wavemeter for accurate frequency determination. All remaining 355 nm radiation and the visible OPO signal beam is removed with a filter (F) prior to directing the light through the photolysis chamber after which it is intercepted by a thermal power meter. A shutter, S, is used to chop the IR light.

The photolysis beam is co-aligned with a second laser that is used to excite OH fluorescence. The fluorescence is detected perpendicular to the flow and laser axes using a scheme similar to that employed on Harvard University's HO_x instrument for the ER-2 airplane [Wennberg *et al.*, 1994b]. The tunable UV light is produced by frequency doubling the output of a dye laser (Lambda Physik, FL3001). The dye laser is pumped by a frequency-doubled, diode-pumped Nd:YAG laser (Spectra Physics) operated at 5 kHz pulse repetition frequency. This radiation is used to excite OH to the first vibrationally excited level of the A state (282 nm). Collisions with nitrogen quench the vibration and fluorescence is observed from the ground vibrational state. The fluorescence is collected on a lens, collimated, and directed through a high efficiency interference filter to separate the signal (310 nm) from the laser scatter (282 nm). A photomultiplier tube (EMR, bialkali) is used in photon counting mode. OH densities as small as 10^4 cm^{-3} can be detected with 1-3 mW of UV. We have tested the sensitivity of the system to changes in the alignment of the two laser beams and have assured that the observed variation in this alignment does not alter the results presented here.

For the HO_2NO_2 system, we can observe photodissociation cross sections ($\Phi \times \sigma$) as small as 2×10^{-24} cm^2. At 300 mW photolysis power, this cross section corresponds to a signal of about 20 counts s^{-1} (cps) on top of a background of 100-200 cps under typical flow tube conditions. The background is produced primarily from thermal decomposition of HO_2NO_2 and is measured by continuously chopping the photolysis beam.

We have observed the temporal evolution of the OH signal following photolysis of the HO_2NO_2 and it is consistent with the time scale for conversion of HO_2 to OH followed by loss of OH via reaction with HO_2NO_2 and advection out of the probe beam. The OH signal is observed to decay with an e-folding time of about 1.5 ms. The short time scale significantly limits the linearity of the photon counting system and for many of the results presented here, the intensity of the UV had to be greatly attenuated to maintain signal rates below ~ 300 cps where counting linearity has been assured.

In separate experiments, we have determined the cross sections for numerous combination bands of HO_2NO_2 in the near IR. A dual UV/IR experiment was first performed to obtain cross sections of the 2nd overtone of the OH stretch ($3\nu_1$). This results of this study, published by Zhang *et al.*, [2000a], are in agreement with liquid phase measurements by Fono *et al.*, [1999]. Using FTIR absorption spectroscopy, we have also obtained the cross sections of other combination bands in the spectral region of interest by scaling to the fundamental band intensities determined by May and Friedl, [1993]. Finally, we have observed HO_2 production from the OH stretch overtone ($2\nu_1$) + OH bend (ν_3) at 1200 nm; the OH stretch overtone ($2\nu_1$) at 1400 nm; and a transition at 1600 nm (6255 cm^{-1}) perhaps a combination of the OH stretch and OH bend ($\nu_1 + 2\nu_3$).

Using the apparatus described above, we have examined the region between 800 and 2000 nm. Near 990 nm, we have scanned the photolysis laser over the 2nd overtone ($3\nu_1$) and observed HO_2 production. This transition is expected to be fully dissociative ($\Phi_{3\nu1}$ = 1) as it lies some 20 kJ/mole above D_o and the lifetime of the excited molecule is calculated to be very short [Donaldson *et al.*, 1997]. RRKM calculation support this suggestion. Several additional lines of evidence suggest that $\Phi_{3\nu1}$ is indeed very close to unity. First, the shape of the action spectrum closely matches the shape of the absorption spectrum. In particular, the hot bands, observed between 980 and 985 nm have the same yield (ratio of action to absorption) as does the band center (Figure 2A). Second, the ratio of the HO_2 signal for this transition to that of the 1200 nm transition scales as the ratio of their cross sections. This is unlikely to be the case unless both transitions lie above D_o in energy and are completely dissociative. HO_2NO_2 experiences collisions on time scale of ~ 150 ns $torr^{-1}$ and for the pressures employed here (2-25 torr) the lifetime of the vibrationally excited molecule must be hundreds of nanoseconds if collisional quenching is to be effective at removing the large excess energy (~2500 cm^{-1}) provided by excitation of $3\nu_1$.

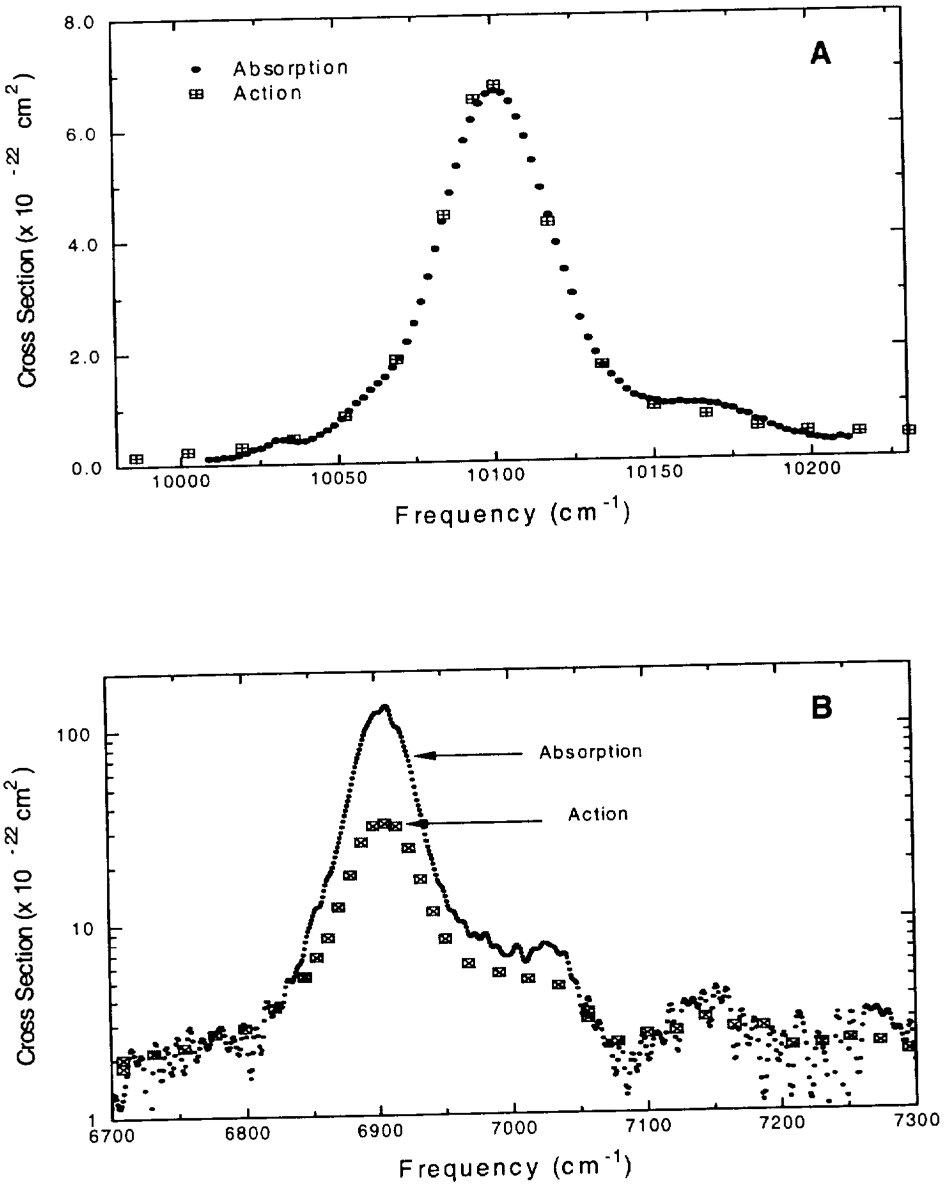

Figure 2. A) The action and absorption cross sections for the 2nd OH overtone ($3\nu_1$) of HO_2NO_2. The peak heights are normalized; the quantum yield is the same throughout the band. B) The action and absorption cross sections for the OH overtone ($2\nu_1$). The quantum yield is 25% as large as $3\nu_1$ in the center of the band but increases on the wings. The hot bands have quantum yield approaching one.

Although the thermochemistry of HO_2NO_2 is still quite uncertain, recent studies suggest that D_o is 94 ± 5 kJ/mole (1270 ± 80 nm) [Miller *et al.*, 1999; Zabel, 1995]. Nevertheless, we have observed significant HO_2 production from HO_2NO_2 at wavelengths as long as 1600 nm. This HO_x production cannot be attributed to two photon effects as we have carefully checked the linearity of the system. The measured quantum yields are also independent of the concentration of NO eliminating the possibility that the HO_2 production results from the reaction of NO with vibrationally-excited HO_2NO_2. Experiments are performed by measuring the HO_2 signal at all wavelengths relative to the signal obtained at the center of the 2nd overtone. The ratio $\Phi_\lambda \times \sigma_\lambda / \Phi_{3v1} \times \sigma_{3v1}$ is then determined after correcting for variation in the laser beam intensity. We have examined this ratio for the 1200 nm transition and the overtone as a function of pressure (2 - 25 torr) and find no change.

As shown in Figure 2B, the quantum yield for the overtone of the OH stretch ($2v_1$) approaches unity for the hot bands that lie to the blue of the band head (note again that the absolute magnitude of the quantum yield is predicated on the assumption that $\Phi_{3v1} = 1$). Within the overtone itself, the quantum yield is observed to decrease, reaching a minimum of 25% at band center. Note that the OPO has a frequency width of approximately 1 cm^{-1} (0.2 nm at this wavelength) and so we are fully resolving the changes in the quantum yield. We have also observed HO_2 production from the 1600 nm band. Although quite weak, our initial measurements suggest that the quantum yield for this transition is between 2 and 4%. This is a surprisingly high yield; the photon energy is 1500 cm^{-1} less than D_o. In regions far from these transitions, no action signal is observed and we can place a limit on the cross sections of $< 2 \times 10^{-24}$ cm^2.

The variation of the quantum yield with wavelength suggests that internal rotational and vibrational energy contribute significantly to bond fissure. At the temperature that this experiment was performed (278 K), HO_2NO_2 contains ~ 450 cm^{-1} of internal vibrational energy. In addition, as has been observed in molecules such as O_3 [Michelsen *et al.*, 1994] and NO_2 [Roehl *et al.*, 1994], some fraction of the nearly 3/2 kT (280 cm^{-1}) of rotational energy may also be coupled into the reaction coordinate.

Photodissociation spectra of four selected bands, the $3v_1$ OH-stretch overtone, a combination band assigned to $2v_1 + v_3$, the $2v_1$ OH-stretch overtone, and a second

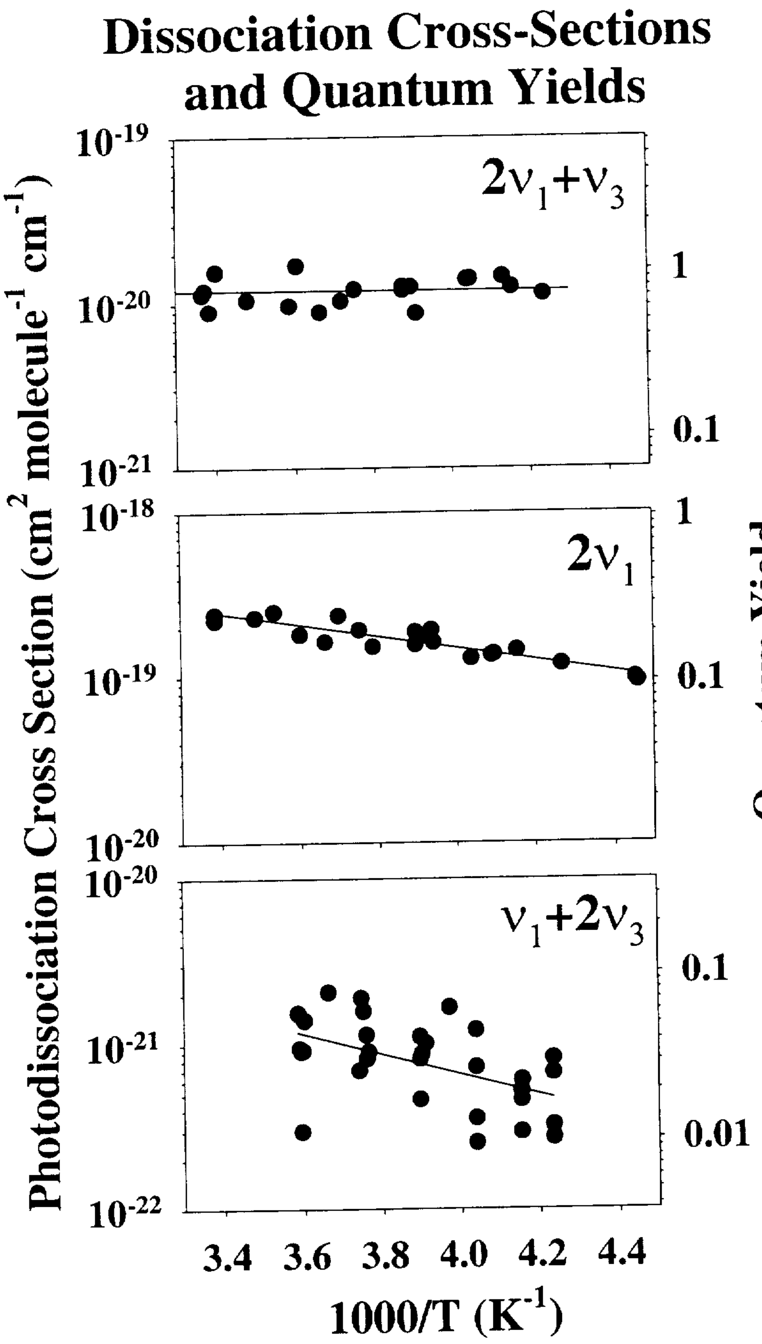

Figure 3. Photodissociation cross sections and quantum yields for three purely vibrational transition of HO_2NO_2.

combination transition tentatively assigned to $\nu_1+2\nu_3$, were examined as a function of temperature. All these bands were also observable in the FTIR absorption spectrum of HNO_4. After accounting for variations in the IR laser power and removing the background signal due to the UV probe laser scatter, UV photolysis of HNO_4, and HNO_4 thermal decomposition, integrated band dissociation cross sections were calculated relative to $3\nu_1$ (3.3×10^{-20} cm^2 $molecule^{-1}$ cm^{-1}) at each temperature. To minimize the effect of small drifts in the probe laser power and/or changes in the HNO_4 concentration on the relative intensity measurements, all photodissociation scans were immediately followed and/or preceded by the scans over the $3\nu_1$ reference band. While the normalized intensity of the $2\nu_1 + \nu_3$ combination band is independent of temperature, both $2\nu_1$ and $\nu_1 + 2\nu_3$ combination band exhibited strong temperature dependence. This dependence is demonstrated for $2\nu_1$ in Figure 3, which shows the normalized photodissociation spectra taken at 283, 244, and 224 K.

Solar radiation that excites the vibrational combination bands of HO_2NO_2 significantly contribute to the photodissociation of this molecule (Figure 4). The overtone of the OH stretch ($2\nu_1$) is primarily responsible despite the low quantum yield because the integrated cross section of this transition is quite high - ~16 times larger than that of the 2nd overtone and 20 times larger than the 1200 nm combination band.

The increased loss rate for HO_2NO_2 significantly reduces the calculated concentration of HO_2NO_2 in the UTLS. This impacts the ozone photochemistry by reducing the loss rate of OH by the reaction:

$$OH + HO_2NO_2 \rightarrow H_2O + O_2 + NO_2.$$

Calculated HO_2 concentrations are 5-40% larger when this process is included [Salawitch et al., 2002].

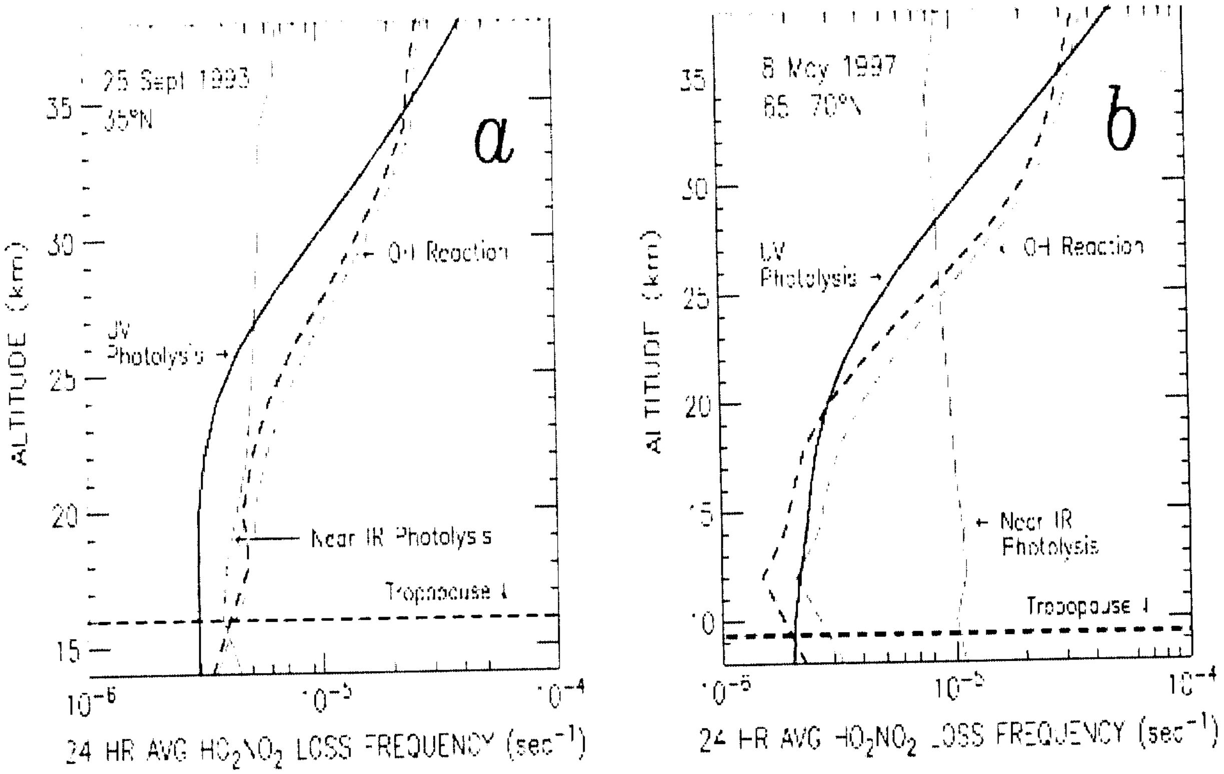

Figure 4. Calculated loss frequencies for HO2NO$_2$ by reaction with OH, and photolysis in the UV and IR. At high latitude, the IR photolysis dominates the loss [Salawitch et al., 2002].

References

Donaldson, D.J., *et al.*, 1997: Atmospheric radical production by excitation of vibrational overtones via absorption of visible light, *Geophys. Res. Lett.*, **24**, 2651.

Fono, L., Donaldson, D.J., Proos, R.J., and Henry, B.R., 1999: OH overtone spectra and intensities of pernitric acid, *Chem. Phys. Lett.*, **311**, 131.

Kenley, P.L. Trevor, and B.Y. Lan, 1981: Preparation and thermal decomposition of pernitric acid ($HOONO_2$) in aqueous media, *J. Am. Chem. Soc.*, **103**, 2203.

May, R.D. and Friedl, R.R., 1993, Integrated band intensities of HO_2NO_2 at 220K, *J. Quant. Spectrosc. Radiat. Transfer*, **50**, 257.

Michelsen, H.A., Salawitch, R.J., Wennberg, P.O., and Anderson, J.G., 1994: Production of O (^{1}D) from photolysis of O_3, *Geophys. Res. Lett.*, **21**, 2227.

Miller, C.E., Lynton, J.I., Keevil, D.M., Francisco, J.S., 1999, Dissociation Pathways of Peroxyacetyl Nitrate, *J. Phys. Chem.*, **103**, 11451.

Roehl, C.M., Orlando, J.J., Tyndall, G.S., Shetter R.E., Vazquez, G.J., Cantrell, C.A., Calvert, J.G., 1994: Temperature-dependence of the quantum yields for the photolysis of NO_2 near the dissociation limit, *J. Phys. Chem.*, **98**, 7837.

Roehl, C.M., S.A. Nizkorodov, H. Zhang, G.A. Blake, P.O. Wennberg, Photodissociation of peroxynitric acid in the near IR *J. Phys. Chem. A*, 106, 3766 , 2002

Salawitch R.J., *et al.*, 1994: The diurnal variation of hydrogen, nitrogen, and chlorine radicals: Implications for the heterogeneous production of HNO_2, *Geophys. Res. Lett.*, **21**, 2547.

Salawitch R.J., P.O. Wennberg, G. Toon, and J.-F. Blavier 2002: Near IR Photolysis of HO_2NO_2: Implications for HO_x, *Geophys. Res. Lett.*, *in press*.

Wennberg P.O., *et al.*, 1994a, Removal of stratospheric O_3 by radicals - in situ measurements of OH, HO_2, NO, NO_2, ClO, and BrO, *Science*, **266**, 398.

Wennberg, P.O., *et al.*, 1994b: An aircraft-borne, laser induced fluorescence instrument for the in situ detection of hydroxyl and hydroperoxyl radicals, *Rev. Sci. Instrum.*, **65**, 1858.

Wennberg, P.O. *et al.*, 1999: Twilight observations suggest unknown sources of HO_x, *Geophys. Res. Lett.*, **26**, 1373.

Wu S., Blake G.A., Sun Z.Y., Ling J.W., 1997: A Simple, High Performance Type II β-BaB_2O_4 OPO, *Applied Optics*, 36: 5898-5901.

Zabel, F., 1995: Unimolecular decomposition of peroxynitrates, *Z. Phys. Chem.*, **188**, 119.

Zhang, H., Roehl, C.M., Sander, S.P., and Wennberg P.O., 2000a: Intensity of the second and third OH overtones of H_2O_2, HNO_3, and HO_2NO_2, *J. Geophys. Res.*, **105**, 14593.