OH(A) Production in the 193-nm Photolysis of HONO

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The formation of OH(A) and OD(A) in the 193-nm photolyses of HONO and DONO with a low quantum yield of about 10^{-5} is reported. The rotational population of OH(A) can be approximated by a Boltzmann distribution with a temperature of 650 K. It is compared with the predictions of the impulsive and statistical models and is found to be close to the latter. A reinvestigation of the absorption spectrum for HONO between 185 and 270 nm and a comparison of the OH(A-X) fluorescence intensities excited in the 193-nm photolyses of nitric and nitrous acids are also reported.

Introduction

Recent work from this laboratory¹ has shown that the intense OH(A) fluorescence observed in the 193-nm photolysis of nitric acid² is generated in the secondary photolysis of an intermediate species.

> $HNO_3 + 2h\nu(193) \rightarrow OH(A) + products$ (1)

$$OH(A) \rightarrow OH(X) + h\nu_{fl}$$
 (2)

It was proposed that this intermediate species is an excited state of HONO, probably its lowest triplet state.^{1b} In a previous work,² it was shown that this OH(A) fluorescence can be used to detect HNO₃ in air at mixing ratios of a few parts per billion. Since nitric acid can be found at about these concentration levels in polluted urban atmospheres,³ work is currently in progress to develop a practical detection technique based on this fluorescence. If another component of the polluted atmosphere were also to yield OH(A-X) fluorescence following excitation at 193 nm, an interference would be caused in the detection of nitric acid. One likely candidate for such interference is HONO since (a) HONO is a known atmospheric pollutant,⁴ (b) it can have a mixing ratio similar to that for $HNO_{3}^{3,4}$ (c) the major known photodissociation channel,⁵ reaction 3, is sufficiently exothermic at 193 nm to allow

$$HONO + h\nu \rightarrow OH + NO$$
(3)

the formation of OH(A),⁶ and (d) it has been proposed that 193-nm photolysis of excited triplet HONO yields OH(A).^{1b} The work we report here was undertaken to determine if OH(A) is produced in the 193-nm photolysis of ground-state HONO. However, such a study is not straightforward because HONO cannot be prepared in pure form⁵ and in particular exists in equilibrium with a small partial pressure of $\dot{HNO}_{3.7}$ In addition, there seems to be little information available about the absorption cross section of HONO below 200 nm.

The UV absorption spectrum of HONO consists of a diffuse structured band between 300 and 390 nm⁸ and a stronger

structureless band beginning around 270 nm and extending to shorter wavelengths.⁹ The quantum yield for dissociation in the low-energy band has been estimated to be one.^{10,11} In addition, Cox^{11} has determined that the dominant reaction for $330 < \lambda < \lambda$ 380 nm is reaction 3 with a quantum yield for OH(X) production of 0.92 ± 0.16 at 365 ± 5 nm.⁹ The formation of electronically excited hydroxyl radicals in reaction 3 is energetically possible for $\lambda < 204$ nm while the production of NO* requires wavelengths shorter than 165 nm.⁶

Although there seem to be no previous reports of the formation of electronically excited products in the photolysis of HONO, some conclusions can be reached based on analogy with methyl nitrite. Tanaka and co-workers¹² have reported the formation of electronically excited methoxy radicals (OCH_3^*) in the photolysis of methyl nitrite at wavelengths shorter than the thermodynamic limit of 206 nm. They have also observed and analyzed the emission spectrum of the OCH₃(A-X) fluorescence excited in the 193-nm photolysis of CH₃ONO and find that the OCH₃(A) is "highly rotationally and vibrationally excited".¹³ Lahmani and co-workers¹⁴ have studied the production of electronically excited nitric oxide using synchrotron radiation.

This paper reports the observation of OH and OD (A-X) emission in the 193-nm photolyses of HONO and DONO. In addition, we report the quantum yield for OH(A) production at 193 nm, a quantitative comparison of the OH(A-X) fluorescence signal strengths excited in the 193-nm photolyses of nitric and nitrous acids and a reinvestigation of the absorption spectrum of HONO between 185 and 270 nm.

Experimental Section

The photolyses of HONO and DONO were carried out in a stainless steel cell equipped with Spectrosil windows, using the unfocussed output of an excimer laser (EMG 501, Lambda Physik) operating with ArF (193.3 nm). The emission spectra were recorded with a 0.5-m monochromator (Minuteman 305) and photomultiplier (EMI 9789 QB). The output of the photomultiplier was processed by a boxcar integrator (PAR 162/164) and strip chart recorder. Calibrated dielectric filters (Acton Research) were used to vary the fluence of the laser in some experiments. A Gentec ED 500 power meter was used to determine the absolute fluence.

The absorption spectrum of HONO was measured by using the same cell (path length 13 cm) and monochromator with a D_2 lamp (Hanau, D-200) as the light source. For these experiments,

^{(1) (}a) Kenner, R. D.; Rohrer, F.; Stuhl, F. Chem. Phys. Lett. 1985, 116, 374. (b) Kenner, R. D.; Rohrer, F.; Papenbrock, Th.; Stuhl, F. J. Phys. Chem. 1986, 90, 1294.

⁽²⁾ Papenbrock, Th.; Haak, H. K.; Stuhl, F. Ber. Bunsenges. Phys. Chem. 1984, 88, 675.

^{(3) (}a) Pitts, Jr., J. N.; Winer, A. M.; Harris, G. W.; Carter, W. P. L.; Tuazon, E. C. Environ. Health Perspect. 1983, 52, 153. (b) Walega, J. G.; Stedman, D. H.; Shetter, R. E.; Mackay, G. I.; Iguchi, T.; Schiff, H. I. Environ. Sci. Technol. 1984, 18, 823.

⁽⁴⁾ Kessler, C. Dissertation, Universität zu Köln, 1984, and references therein

⁽⁵⁾ Okabe, H. Photochemistry of Small Molecules; Wiley: New York, 1978

⁽⁶⁾ Stull, D. R.; Prophet, H. JANAF Thermochemical Tables, 2nd ed.; (7) Ashmore, P. G.; Tyler, B. J. J. Chem. Soc. 1961, 1017

^{8) (}a) Melvin, E. H.; Wulf, O. R. J. Chem. Phys. 1935, 3, 755; (b) King, G. W.; Moule, D. Can. J. Chem. 1962, 40, 2057.

⁽⁹⁾ Cox, R. A.; Derwent, R. G. J. Photochem. 1976/77, 6, 23

 ⁽¹⁰⁾ Johnston, H. S.; Graham, R. Can. J. Chem. 1974, 52, 1415.
 (11) Cox, R. A. J. Photochem. 1974, 3, 175.

⁽¹²⁾ Ohbayashi, K.; Akimoto, H.; Tanaka, I. J. Phys. Chem. 1977, 81, 798.

⁽¹³⁾ Ebata, T.; Yanagishita, H.; Obi, K.; Tanaka, I. Chem. Phys. 1982, 69, 27.

^{(14) (}a) Lahmani, F.; Lardeux, C.; Lavollée, M.; Solgadi, D. J. Chem. Phys. 1980, 73, 1187. (b) Lahmani, F.; Lardeux, C.; Solgadi, D. Ibid. 1980, 73, 4433.

the space between the lamp and the cell was flushed with N_2 , the monochromator was evacuated, and an EMR 541N-09-14 photomultiplier was used. The output signal of the photomultiplier was passed through an amplifier-discriminator and the pulses were counted and stored by a multichannel analyser (Tracor Northern TN1710). The absorbance, $A(\lambda)$, was recorded as a function of wavelength by scanning the monochromator through the desired wavelength range while recording the number of photons detected during the given dwell time, once without sample in the cell, $I_0(\lambda)$, and once with sample in the cell, $I(\lambda)$. These data were then substituted into eq 4 to give the absorbance. Since other species

$$A(\lambda) = \ln \left(I_0(\lambda) / I(\lambda) \right) \tag{4}$$

which absorb in the wavelength region of interest were unavoidably present in the HONO samples (NO, NO₂ etc.), $A(\lambda)$ was measured for each of these species under the same experimental conditions as used for the HONO sample (see Results section). The absorption of HONO at each wavelength was then obtained by subtracting the sum of these measured absorbances from the total absorbance for the mixture.

As a check, the absorption cross sections for HONO were measured at 193.3 and 210 nm. I_0 and I were measured at each of these wavelengths at a resolution of 0.38 nm for both static and flowing conditions. For these experiments, the corrections for the absorbance of NO2 was made using literature values for its cross section^{10,15} and the concentration determined separately by its absorption at 400 nm. The absorbances of NO^{16} and H_2O^{17} are negligible at these wavelengths.

To determine the quantum yield for the production of OH(A)in reaction 5, ϕ_5 , one must determine the number of photons

$$HONO + h\nu(193) \rightarrow OH(A) + NO(X)$$
 (5)

absorbed in the observation volume, N_{ph} , and the number of OH molecules formed in the A state in the same volume, $N_{OH(A)}$. N_{ph} was determined by using the absorption cross section at 193 nm, the measured fluence of the laser and the concentration of HONO determined by pH titration (with the assumption that no decomposition of the nitrous acid occurred upon flowing into the cell). $N_{OH(A)}$ was determined by using eq 6, where G is the correction

$$N_{\rm fl} = N_{\rm OH(A)} S_{\rm m} G(\tau_0^{-1} / \tau^{-1}) \tag{6}$$

for geometrical factors and τ_0 is the natural lifetime of OH(A) $(\tau_0 \sim 850 \text{ ns}^{18})$. The term (τ_0^{-1}/τ^{-1}) corrects for the fraction of OH(A) which does not fluoresce due to electronic quenching. $\tau^{-1} = \tau_0^{-1} + \sum_i k_i n_i$ where k_i is the quenching rate constant of OH(A) by a gas of concentration n_i . The integrated fluorescence intensity, I_{fl} , and reciprocal lifetime, τ^{-1} , were measured by using a transient recorder (Biomation 8100) interfaced to a microcomputer as described previously.^{1b} $N_{\rm fl}$, the number of fluorescence photons emitted per laser shot in the observation volume, was obtained by dividing $I_{\rm fl}$ by the average area of the signal from one photon as registered by the transient recorder. The detection efficiency, S_m , of the monochromator-photomultiplier combination (Jobin-Yvon H25, EMI 9789 QB) was determined by using a calibrated D₂ lamp (Optronic Laboratories, Model UV-40). The value of ϕ_5 was then obtained as the quotient of $N_{OH(A)}$ and N_{ph}

As stated earlier, HONO cannot be prepared in pure form. For the photolysis experiments we required a source of HONO with very low contamination by other precursors for OH(A) which in principle means HNO₃. (The 193-nm photolysis of water vapor with an unfocussed laser does not yield OH(A).²) On the other hand, for the absorption experiments we required known concentrations for HONO and the other species which absorb in the wavelength range of interest. To meet these requirements, we have used two methods to prepare HONO in this work. Method I was based on the reaction of aqueous NaNO2 with sulfuric acid and was used in two variations. In the first variation, Ia, 25 mL of 20% by volume H₂SO₄ in H₂O was added to 50 mL of 0.9 M aqueous NaNO₂. Both solutions were cooled to 273 K before mixing and the resulting solution was kept in an ice bath. The evolved gases were pumped directly through the cell. This method appears to give HONO samples with very low contamination by HNO_3 and relatively low $[NO_2]$. In the second variation, Ib, the solutions were prepared in the same way and nitrogen was bubbled through the solution at atmospheric pressure. The resulting stream containing HONO was either titrated or passed through the photolysis cell. DONO was made by method Ia, substituting D_2SO_4 and D_2O for their protonated analogues.

Method II makes use of equilibrium 7 and has been used in

$$NO + NO_2 + H_2O \rightleftharpoons 2HONO \tag{7}$$

many previous studies of HONO. Small measured amounts of NO₂ and H₂O were added to about 650 Torr of NO in a 4-L glass bulb and the mixture was allowed to equilibrate for 18 h. The equilibrium concentration of NO2 was then determined from its absorbance at 400 nm (measured in a 1.1 cm path length gas cell with a Perkin Elmer 124 UV-vis spectrometer) and the absorption cross section from Johnston and Graham¹⁰ (which agrees with the value we have determined in separate experiments). The partial pressure of the HONO in the mixture could be calculated from the known starting concentrations of H_2O and NO, the measured equilibrium concentration of NO_2 and the known equilibrium constants for equilibria 7-9.19 This equilibrium

$$NO + NO_2 \rightleftharpoons N_2O_3 \tag{8}$$

$$NO_2 + NO_2 \rightleftharpoons N_2O_4$$
 (9)

mixture was flowed directly into the photolysis cell at total pressures of a few Torr. Since the reverse of reaction 7 is relatively slow,^{19,20} we have assumed that the HONO mixing ratio does not change upon expansion of the equilibrium mixture into the photolysis cell. On the other hand, since equilibria 8 and 9 are established very quickly,^{21,22} the concentrations of N_2O_3 and N_2O_4 in the photolysis cell were too low under the conditions of our experiments to contribute measurably to the absorbance, even when a flowing sample is used.

In order to directly compare the intensities of the OH(A)fluorescence generated in the photolyses of HONO and HNO₃, it was necessary to obtain an HNO₃ sample under conditions similar to those used for the HONO. To reproduce the conditions of the HONO produced by method Ib, we bubbled N₂ through a concentrated aqueous solution of nitric acid at 273 K. This gave a similar acid partial pressure in the nitrogen stream and similar quenching of the OH(A). We found that it was first necessary to flow the N_2 through the solution for several hours. If this were not done, the main acid vapor in the N₂ stream appeared to be HONO, not HNO₃ as expected.

For those experiments in which the concentration of HONO or HNO₃ was determined by titration, the nitrogen stream containing the acid vapor was bubbled through a dilute solution containing a known amount of NaOH and the time necessary to neutralize the OH⁻ was measured. A mass flow controller (Tylan) was used to control the N₂ flow and the progress of the titration was followed with a calibrated glass electrode and pH meter. After titration, the gas flow was directed through the photolysis cell for emission intensity or absorption measurements. The gas stream was then redirected through the alkali solution for a second ti-

The chemicals used in this investigation (with indicated minimum purities) were NaNO₂ (Riedel-de Haën, 98%), H₂SO₄

⁽¹⁵⁾ Baulch, D. L.; Cox, R. A.; Hampson, Jr., R. F.; Kerr, J. A.; Troe, J.; Watson, R. T. J. Phys. Chem. Ref. Data 1980, 9, 295.
(16) (a) Pearse, R. W. B.; Gaydon, A. G. The Identification of Molecular

Spectra, 4th ed.; Chapman and Hall: London, 1976. (b) Guest, J. A.; Lee,

^{1226. (}b) Brzozowski, J.; Erman, P.; Lyyra, M. Phys. Scr. 1978, 17, 507.

⁽¹⁹⁾ Stockwell, W. R.; Calvert, J. G. J. Photochem. 1978, 8, 193.

⁽²⁰⁾ Kaiser, E. W.; Wu, C. H. J. Phys. Chem. 1977, 81, 1701.
(21) (a) Wayne, L. G.; Yost, D. M. J. Chem. Phys. 1951, 19, 41. (b) Hochanadel, C. J.; Ghormley, J. A.; Ogren, P. J. J. Chem. Phys. 1969, 50, 3075.

^{(22) (}a) Grüneisen, E.; Goens, E. Ann. Phys. **1923**, 377, 193. (b) Carrington, T.; Davidson, N. J. Phys. Chem. **1953**, 57, 418 and references therein.



Wavelength / nm

Figure 1. OH(A-X) emission spectrum between 306 and 314 nm observed in the 193-nm photolysis of HONO. Resolution 0.09 nm, cell pressure 145 mTorr (approximately 10% HONO, see text), uncorrected for the detector sensitivity. Spectral assignments based on data of ref 27, labeled by N".

(Riedel-de Haën, 95–97%), H_2O (deionized), D_2SO_4 (Aldrich, 98%, Gold Label), D_2O (Aldrich, 99.8%), NO (Messer Griesheim, 99.8%), NO₂ (Messer Griesheim, 98%), N₂ (Messer Griesheim, 99.99%), NaOH (Riedel-de Haën, 0.1 N solution), and HNO₃ (Riedel-de Haën, 99%).

Results

A spectrum of the OH(A-X) fluorescence excited in the 193-nm photolysis of HONO is shown in Figure 1. This spectrum was obtained at a resolution of 0.09 nm (fwhm) by using HONO prepared by method Ia with a total cell pressure of 0.145 Torr. (On the basis of our results in the experiments involving titrations, we estimate that approximately 10% of this pressure was HONO, with most of the remainder being NO.) We noted that experiments on successive days yielded increasing fluorescence signals, even though we used exactly the same preparation technique and laser fluence. In these experiments, HONO was in superequilibrium concentrations throughout the apparatus. Therefore, a decreased rate of heterogeneous decomposition due to passivation of the surfaces of the flask used in the preparation, the connecting tube, and the valve used to control the gas flow into the photolysis cell would lead to higher HONO concentrations in the cell and this would explain the increased signal strength. Such a passivation of the cell walls was previously reported by Kaiser and Wu.²⁰

A determination of the dependence of the OH(A-X) fluorescence intensity $(I_{\rm fl})$ on the laser fluence (I_{193}) gave a value of 1.0 for *n* in the equation $I_{\rm fl} \propto I_{193}^n$. Since the OH(A) fluorescence intensity from HNO₃ photolysis is high and shows a square dependence on the laser fluence,² the value, n = 1.0, obtained for HONO is good evidence that our sample has very low contamination by HNO₃. (For comparison, earlier experiments using method Ia without cooling the solutions gave n = 1.4.)

Figure 2 shows a spectrum of the OD(A-X) fluorescence excited in the 193-nm photolysis of DONO at a total cell pressure of 0.11 Torr (the partial pressure of DONO is uncertain in this



Wavelength / nm

Figure 2. OD(A-X) emission spectrum between 306 and 314 nm observed in the 193-nm photolysis of DONO. Resolution 0.15 nm, cell pressure 110 mTorr (<10% DONO, see text), uncorrected for the detector sensitivity. Spectral assignments based on data of ref 28, labeled by N".



Wavelength / nm

Figure 3. Absorption spectra of HONO and CH_3ONO between 185 and 270 nm. The solid curve is the absorption spectrum for HONO determined in this work (the error bars indicate the estimated statistical error). The open circles connected by a dotted line are based on the tabulated data for HONO given in ref 9. The dashed curve is the absorption spectrum for CH_3ONO based on the data from ref 14a and 23.

case but should be less than 10%). Only a lower resolution spectrum (0.15 nm) was obtained due to the lower signal intensity (probably caused by insufficient passivation of the preparation apparatus and cell). The fluence dependence was n = 1.05 in this case.

We have determined the absorption spectrum for HONO between 185 and 270 nm at a resolution of 0.38 nm from the measured absorbance of a slowly flowing sample of the equilibrium mixture prepared by method II (initially at a total pressure of 670 Torr) at a cell pressure of 5.1 Torr. Separate absorption spectra were measured for samples of H₂O and a mixture of NO and NO₂ prepared to match the calculated equilibrium concentration of each of these species in the HONO sample mixture. These spectra were subtracted from that obtained above to give the spectrum indicated by the heavy solid curve in Figure 3. At wavelengths where the absorbance of NO is negligible, the HONO contributed 20-50% of the total absorbance. At wavelengths corresponding to NO absorption peaks, this fraction decreased to about 10%. Although we attempted to measure the spectrum down to 170 nm, the results below 185 nm are not included because of a low signal to noise ratio caused by the relatively low intensity of the lamp in this region and the large corrections necessary for the absorbances of NO^{16b} and $H_2O^{.17}$ Since a slight change in the intensity of the lamp during these experiments would cause the absolute absorbance to be uncertain, we have normalized the cross sections to the values we have determined separately at 193.3 and 210 nm. As a further check, we have measured this spectrum over the limited range of 195-240 nm using HONO prepared by method Ia. The results agree with those shown in Figure 3 within the experimental uncertainties. For comparison, we have included in this figure an absorption spectrum based on the tabulated data of Cox and Derwent⁹ (note that somewhat different values are given in their plotted data) and an absorption spectrum for

CH₃ONO based on data from Taylor et al.²³ and Lahmani et al.^{14a} The quantum yield for OH(A) production in the photolysis of HONO, ϕ_5 , was determined at a laser fluence of 13 mJ cm⁻² by using 0.61 Torr of a HONO/N₂ mixture (preparation Ib) with an HONO partial pressure of 9.3 mTorr. An average of 109 photons per laser shot were registered in the wavelength range of 306.5–311.5 nm (which covers almost the entire emission spectrum, see Figure 1). The measured lifetime was 431 ns. (The major quenching molecule is expected to be NO.) When these values are substituted into eq 6, along with the appropriate values for the geometrical factor and the detector efficiency, $N_{OH(A)} =$ 3.5×10^8 per shot in the observation volume of 3 cm³. With the measured cross section at 193 nm ($\sigma(193) = 1.6 \times 10^{-18}$ cm²) and the above laser fluence and concentration, $N_{ph} = 1.9 \times 10^{13}$. This gives $\phi_5 = 1.8 \times 10^{-5}$.

Similar experiments were performed photolyzing 1.99 Torr of the HNO_3/N_2 mixture (HNO₃ partial pressure, 5.3 mTorr) with a laser fluence of 0.76 mJ cm⁻². On average, 151 photons per laser shot were detected by their emission in the wavelength region 306.5-311.5 nm with an observed lifetime of 445 ns. (Note that this wavelength range covers only part of the emission spectrum in this case,² but our interest here is in comparing the signal strengths for the conditions Papenbrock et al.² have used for their calibration curve.) When corrected as before, this gives $N_{OH(A)}$ = 4.6×10^8 . The intensity of the OH(A) fluorescence excited in the photolysis of HNO₃ is proportional to the HNO₃ partial pressure and to the square of the laser fluence.² In order to compare the signal measured for HNO₃ with that measured for HONO, the HNO₃ signal strength must be multiplied by the ratio of partial pressures and the ratio of the squares of the laser fluences. This yields $N_{OH(A)} = 2.3 \times 10^{11}$ which would emit in the indicated wavelength region for 9.3 mTorr of HNO3 at a laser fluence of 13 mJ cm⁻². For these conditions, the signal from HNO_3 is calculated to be about 650 times larger than that from HONO.

Discussion

The absorption spectrum which we have determined is in quantitative agreement with that reported by Cox and Derwent⁹ over the wavelength range of 270–220 nm (see Figure 3). We are, however, unable to reproduce the sharp peak at 215 nm reported by these workers. We know of no other spectra for HONO in this wavelength region with which we can compare our results. We believe that our spectrum is correct for the following reasons:

1. The corrections for the absorbance of NO, NO₂, H₂O, etc. were accomplished by measuring their absorbances under experimental conditions identical with those used for HONO (pressure, path length, light intensity, resolution, detection system, and geometry). The NO and NO₂ were premixed for this measurement to assure the same concentration of N_2O_3 and N_2O_4 . (As stated earlier, these species should have negligible concentration under these experimental conditions but we do not depend on this assumption.) Correction by this method is particularly important for NO as it has a line spectrum and the different bands show varying amounts of saturation at pressures above about 1 mTorr.^{5,16b} Since the absorption bands of NO are clearly evident in our original data, failure to adequately correct the spectrum would lead to either peaks or valleys at the positions of these bands. This is not the case in our spectrum. In particular, we note that the NO(A, $v=1 \leftarrow X$,v=0) band occurs at a wavelength of 215 nm.^{16a} Cox and Derwent⁹ state that they have used the data from Calvert and Pitts²⁴ to correct for the absorption of NO, data which we feel are inadequate for the task. Since the Cox and Derwent data were taken at 5-nm intervals,9 the contours of the NO absorption bands would not be obvious in their spectrum to provide a crosscheck of adequate correction.



Wavelength / nm

Figure 4. Simulated spectra for $OH(A,v=0\rightarrow X,v=0)$ based on the line positions and line strengths from ref 27 convoluted with a triangular slit function assuming a rotational population described by (a) a Boltzmann distribution with a temperature of 650 K, (b) a thermal distribution of the rotational energy given by the impulsive model, and (c) the prior distribution given by the statistical model.

2. We have prepared HONO by two different methods and have obtained the same results in both cases.

3. When one compares the UV absorption spectra of nitric $acid^{25}$ with those of the alkyl nitrates,²⁴ one finds that the band shapes are very similar. However, the wavelengths of the absorption maxima show red shifts, and the absolute cross sections increase with increasing size of the substituent group. Comparing the alkyl nitrites,²⁴ one sees the same trend. By analogy, it therefore seems reasonable that the absorption spectrum for HONO should have the same band shape as CH₃ONO (see Figure 3), but with a smaller absorption cross section and a somewhat shorter wavelength for the peak absorbance.

The absolute value of the absorption cross section which we report depends upon the assumption that there was negligible decomposition of the HONO upon flowing into our cell. While the homogeneous decomposition rate of HONO is very slow, heterogeneous catalysis can have a very large effect.²⁰ We are unable to quantify the magnitude of this effect in our apparatus. Once in the cell, the decomposition rate of HONO seems to be relatively slow as we have been unable to detect changes in the absorbance of a static fill at 210 nm over a period of several minutes. In addition, the value of 1.6×10^{-18} cm² at 193.3 nm is in agreement with the upper limit set in earlier experiments measuring the attenuation of the laser intensity over a 27.5-cm path length using HONO prepared by method Ia.

Comparing the OH and OD(A-X) spectra we have obtained in this work (see Figures 1 and 2) with those observed in the excimer laser photolyses of $HNO_3^{2,1}$ and DNO_3^{26} one sees that the rotational excitation is much lower in the spectra shown here. Since the excess energy is much lower in the one-photon photolysis

⁽²³⁾ Taylor, W. D.; Allston, T. D.; Moscato, M. J.; Fazekas, G. B.; Kozlowski, R.; Takacs, G. A. Int. J. Chem. Kinet. 1980, 12, 231.
(24) Calvert, J. G.; Pitts, Jr., J. N. Photochemistry; Wiley: New York, 1967.

^{(25) (}a) Johnston, H.; Graham, R. J. Phys. Chem. 1973, 77, 62. (b) Suto, M.; Lee, L. C. J. Chem. Phys. 1984, 81, 1294 and references therein.

⁽²⁶⁾ Kenner, R. D.; Rohrer, F.; Stuhl, F., unpublished results.

of HONO than in the two-photon photolysis of HNO₃, this is not surprising. We have simulated the fluorescence spectra from HONO assuming a Boltzmann distribution in the rotational population with the temperature (T_{rot}) as a parameter. For the OH(A-X) fluorescence we have used the line positions and line strengths from the work of Goldman and Gillis²⁷ convoluted with a triangular slit function. The resulting spectrum for $T_{rot} = 650$ K is shown in Figure 4a. As one can see, the agreement with the spectrum in Figure 1 is quite good. Similar simulations for OD, using the line positions from the work of Clyne et al.²⁸ and line strengths based on the formulas of Bennett,²⁹ give an equally good fit to the spectrum in Figure 2 for $T_{rot} = 650$ K. These temperatures can be compared with $T_{rot} = 3750$ K for OH(A) formed in the 193-nm photolysis of HNO₃.^{1b}

To further elucidate the nature of the photodissociation process, we have simulated the spectra to be expected for the OH(A-X)fluorescence in the 193-nm photolysis of HONO based on two simple models: the impulsive³⁰ and statistical models.³¹ Each of these models describes the distribution of the available excess energy of the photodissociation process among the various states of the photofragments. Nitrous acid exists as an equilibrium mixture of two rotamers, cis and trans,³² in a ratio of 1:2.3 at room temperature.³³ We calculated the excess energy for reaction 3 based on a weighted average of the thermodynamic values for the two rotamers⁶ and obtained a value of 2550 cm⁻¹. Since the parent molecule is initially at room temperature we added to this value the average rotational energy of HONO at 298 K. (Since the lowest fundamental vibrational frequency of nitrous acid is 540 cm⁻¹,³⁴ we neglected the vibrational excitation at room temperature.) We then obtained a total excess energy of 2860 cm^{-1} .

In the impulsive model,³⁰ all the excess energy is assumed to appear initially as relative translation of the two departing photofragments. Part of this energy is then channelled into rotation and vibration of the separated fragments. Agreement with this model is usually taken to imply a direct photodissociation process. Figure 4b shows the expected spectrum based on the excess energy, the H–O–N bond angle from Finnigan et al.,³⁵ and the assumption that the calculated rotational energy of 100 cm⁻¹ is distributed in a thermal manner. It is clearly evident that, in this model, too little energy is going into rotation to explain our results.

In the statistical model, it is assumed that all energetically accessible states are equally probable and are populated strictly according to their statistical weight.³¹ Agreement with the sta-

tistical model is usually taken to imply a "slow" dissociation with time for energy redistribution. Figure 4c shows the expected spectrum based on this model (prior distribution). In this case, the agreement with the experimental spectrum is much better, especially when one considers that there may be some relaxation of the rotational distribution under the conditions used to measure the experimental spectrum. However, any effect of relaxation is expected to be small since the major collision partners, NO, NO₂, and H₂O are very efficient electronic quenchers.³⁶

For OCH₃(A) formed in the 193-nm photolysis of CH₃ONO, Ebata et al.¹³ found that the vibrational distribution agreed with the predictions of the statistical model. These workers were unable to analyze the rotational distribution due to spectral congestion. In addition, Lahmani et al.^{14b} have found that the vibrational distribution of the NO(A) photofragment formed in the vacuum-UV photolysis of CH₃ONO is in agreement with the statistical model.

The theoretical energy surfaces obtained by Larrieu et al.³⁷ for the photodissociation of HONO in a coplanar fragmentation show that all electronic states of HONO which are energetically accessible with one ArF laser photon correlate smoothly and without barriers to ground state OH and NO. The production of OH(A) must then involve a change of potential surface and might therefore be expected to have a low probability. This is in agreement with the very small quantum yield we have determined for this dissociation channel. In addition, since the quantum yield is so low, there would not seem to be any fundamental disagreement between the continuous absorption spectrum which implies a direct photodissociation and the observation of a near-statistical distribution of the excess energy among the rotational degrees of freedom.

Finally, we wish to consider the possible interfering effect of HONO for the detection of HNO₃ in air, which was one of the chief aims of this work. For their calibration curve, Papenbrock et al.² have used an interference filter centered at 309 nm with a bandwidth of 5 nm to detect the OH(A) fluorescence. (This covers only about half the total emission.) This wavelength range is the same as that which we have used in these experiments to determine the relative intensities. However, a typical laser fluence in their experiments would be about 50 mJ cm⁻², which was approximately 4 times higher than that which we have used. Since the OH(A) fluorescence intensity is proportional to the square of the laser fluence for HNO_{3} ,² but only the first power for HONO, the ratio of the two will be directly proportional to the laser fluence. This correction then yields a value of about 2500 for the ratio of the OH(A) fluorescence from HNO₃ to that from HONO for the typical conditions of Papenbrock et al.² Since HONO and HNO₃ are found at similar mixing ratios in the polluted atmosphere (typically 1-5 ppb^{3,4}), the OH(A) fluorescence excited in the photolysis of HONO will cause negligible interference for the detection of HNO_3 by this method.

Acknowledgment. We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft (SFB 42) and BMFT Grant No. 07045741.

Registry No. OH, 3352-57-6; OD, 13587-54-7; DONO, 13759-76-7; HONO, 7782-77-6; HNO₃, 7697-37-2; N₂, 7727-37-9.

⁽²⁷⁾ Goldman, A.; Gillis, J. R. J. Quant. Spectrosc. Radiat. Transfer 1981, 25, 111.

⁽²⁸⁾ Clyne, M. A. A.; Coxon, J. A.; Woon Fat, A. R. J. Mol. Spectrosc. 1973, 46, 146.

 ⁽²⁹⁾ Bennett, R. J. M. Mon. Not. R. Astron. Soc. 1970, 147, 35.
 (30) (a) Holdy, K. E.; Klotz, L. C.; Wilson, K. R. J. Chem. Phys. 1970,

 ^{(30) (}a) Holdy, K. E.; Klotz, L. C.; Wilson, K. R. J. Chem. Phys. 1970,
 52, 4588. (b) Busch, G. E.; Wilson, K. R. J. Chem. Phys. 1972, 56, 3626.
 (31) (a) Levine, R. D.; Kinsey, J. L. In Atom-Molecule Collision Theory;

Bernstein, R. B., Ed.; Plenum: New York, 1979. (b) Ben-Shaul, A.; Haas, Y.; Kompa, K. L.; Levine, R. D. Lasers and Chemical Change; Springer Verlag: West Berlin, 1981; Springer Series in Chemical Physics Vol. 10.

^{(32) (}a) D'Or, L.; Tarte, P. J. Chem. Phys. 1951, 19, 1064. (b) Jones, L. H.; Badger, R. M.; Moore, G. E. Ibid. 1951, 19, 1599.

⁽³³⁾ Chan, W. H.; Nordstrom, R. J.; Calvert, J. G.; Shaw, J. H. Environ. Sci. Technol. 1976, 10, 674.

⁽³⁴⁾ McGraw, G. E.; Bernitt, D. L.; Hisatsune, I. C. J. Chem. Phys. 1966, 45, 1392.

⁽³⁵⁾ Finnigan, D. J.; Cox, A. P.; Brittain, A. H.; Smith, J. G. J. Chem. Soc., Faraday Trans. 2 1972, 68, 548.

^{(36) (}a) German, K. R. J. Chem. Phys. 1975, 62, 2584. (b) Copeland, R. A.; Dyer, M. J.; Crosley, D. R. J. Chem. Phys. 1985, 82, 4022.

⁽³⁷⁾ Larrieu, C.; Dargelos, A.; Chaillet, M. Chem. Phys. Lett. 1982, 91, 465.