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First Spectroscopic Observation of Gas-Phase HOONO

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A vibrational overtone photodissociation spectrum of HOONO formed in the reaction of OH with NO_2 is reported. Rich vibrational structure, consistent with the existence of several HOONO conformers, is observed. A tentative vibrational assignment of the observed bands is proposed although complete assignment is not possible without further spectroscopic information. The ratio $HOONO/HONO_2$ formed in the reaction of OH with NO_2 is estimated to be about 5% at 253 K and 20 Torr.

Introduction

The three-body association reaction of hydroxyl radical with nitrogen dioxide

$$OH + NO_2 + M \rightarrow HONO_2 + M \qquad (1a)$$

is one of the most important processes in the chemistry of the Earth's lower atmosphere.[1] By sequestering HO_x and NO_x into the more chemically inert and photochemically stable nitric acid, this reaction terminates several important catalytic cycles involving odd-hydrogen and odd-nitrogen radicals, and directly affects the stratospheric and tropospheric ozone budgets. Detailed knowledge of both the mechanism and kinetics of reaction 1a is, therefore, of critical significance for understanding atmospheric photochemistry.

Although the kinetics of reaction 1 has been a subject of numerous studies under a variety of pressure and temperature conditions,[2,3] there still is a surprising amount of disagreement between studies performed at high and low pressure. It has been speculated[4] that part of this disagreement may arise from a possible reversible side branch to reaction 1,

$$OH + NO_2 + M \leftrightarrow HOONO + M \qquad (1b)$$

which results in a weakly bound adduct of OH and NO_2. Indeed,

the product branching ratio in reaction 1 and the unimolecular decomposition rate of the implicated HOONO intermediate can have a drastic effect on the apparent rate of OH disappearance in kinetic experiments, such as polyexponential and/or isotope specific OH removal.[5]

Golden and Smith[4] analyzed the available kinetic data for reaction 1 using a RRKM approach and concluded that the k_{1b}/k_{1a} branching ratio may be as high as 15% under typical atmospheric conditions, and substantially larger at higher total pressures. On the contrary, Matheu and Green[6] concluded that reaction 1b is insignificant under all relevant atmospheric conditions. Probably the strongest experimental evidence for reaction 1b was presented in a recent report by Donahue et al.,[5] who studied the kinetics of reaction 1 using isotopically labeled OH. Indirect experimental evidence of HOONO formation was also obtained from the observation of a double-exponential decay of OH in excess NO_2.[7] A direct spectroscopic technique for observation of HOONO could clearly provide a much more rigorous experimental constraint for the mechanism of reaction 1. Much to the frustration of experimentalists, however, two major attempts to detect HOONO in reaction 1 and, in fact, in several other reactions thought to produce HOONO in the gas phase were unsuccessful.[8,9]

Direct observation of HOONO vibrational bands in solid Argon matrixes[10−12] and strong evidence for the transient existence of HOONO in aqueous solutions[13−17] proves beyond suspicion that this molecule is not a figment of the theoretical chemists' imagination. Indeed, HOONO is expected to be bound by as much as 18.8 kcal/mol[18] and have at least three stable,

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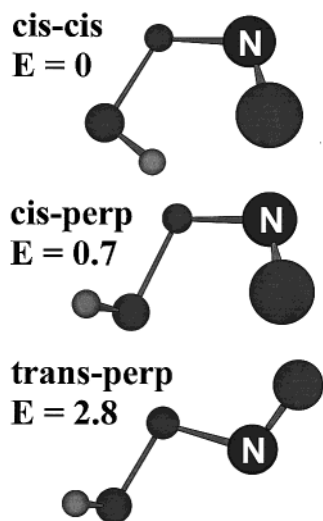
Figure 1. Lowest energy conformers of HOONO. The structures and relative energies of the cis-cis, cis-perp, and trans-perp conformers (in kcal/mol) are taken from ab initio calculations of ref 19. In this notation, the first and second labels refer to the ONOO and NOOH torsional angles, respectively.

nearly isoenergetic conformers differing mostly in the magnitudes of their equilibrium HOON and OONO torsional angles[18−20] (Figure 1). The failure to observe HOONO in the previous experiments must therefore have chemical or dynamical origins.

In this Letter, we report the first direct spectroscopic observation of HOONO produced in reaction 1 and an experimental estimate of the branching ratio k_{1b}/k_{1a}. This measurement takes advantage of the vibrational predissociation spectroscopy approach famous for its high degree of sensitivity and selectivity in spectroscopic studies of weakly bound van der Waals and ionic complexes.[21,22] The main idea is to use vibrational overtone excitation in assisting the decomposition of HOONO back into the original components:

$$HOONO + h\nu \rightarrow HOONO(2\nu_1) \rightarrow OH + NO_2 \quad (2)$$

wherein the resulting OH photofragments are sensitively detected with laser-induced fluorescence (LIF) against essentially no background other than the unreacted OH.

Experimental Section

The experimental setup is similar to the one described in our recent publication on the near-infrared photolysis of peroxynitric acid (PNA ≡ HO$_2$NO$_2$)[23] and only the most pertinent information is provided here. A tunable pulsed OPO laser (2 cm^{-1} resolution; 1 mJ/pulse; 0.3 cm beam diameter) supplies radiation in the frequency range of the first ($2\nu_1$) and second ($3\nu_1$) OH stretching overtones. OH is detected by LIF in the A$^2\Sigma \leftarrow$ $^2\Pi$ band excited by a copropagating tunable dye laser near 282 nm (≪1 μJ/pulse; 0.2 cm beam diameter) in a single photon counting regime. For time-resolved pump−probe experiments, the pulse repetition rate of both lasers is set at 100 Hz and the delay between them is scanned. In the integration mode, which is occasionally used for acquiring spectra, a 6400 Hz comb of probe laser pulses is generated, shifted from the pump laser comb by a known variable delay. In both cases, the gated counting window of the photon counter is locked onto the probe laser pulse, with the gate width (2−4 μs) comfortably accommodating several OH fluorescence lifetimes (≈500 ns[24]). To minimize the saturation of the counting electronics the count rate is kept below 0.05−0.1 counts/gate.
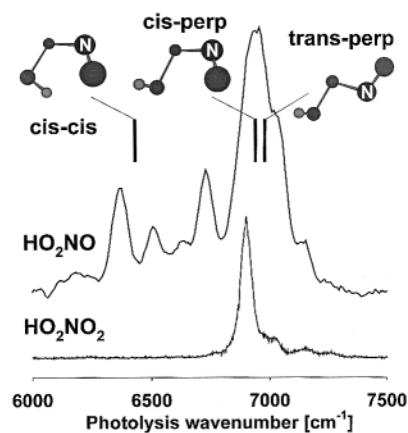

Figure 2. Photodissociation spectrum of HOONO in the first OH stretching overtone region. The strongest bands at 6365 and 6935 cm^{-1} are tentatively assigned to the $2\nu_1$ vibrations of the cis-cis and {cis-perp + trans-perp} conformers of HOONO, respectively. The corresponding anticipated positions of HOONO overtones estimated from the matrix isolation spectra are indicated by vertical bars. The spectrum of PNA, which consists of a single strong $2\nu_1$ band at 6900 cm^{-1} and weaker combination bands at higher frequencies, is also shown for comparison.

OH is produced in a microwave discharge of H$_2$ in a large excess of either helium or argon. The flow coming out of the microwave cavity is mixed with a flow of 0.7% NO$_2$ in N$_2$ and directed in either a FTIR spectrometer or photolysis/LIF chamber maintained at 253 K. The flow conditions are chosen to ensure that all H-atoms are converted into OH

$$H + NO_2 \rightarrow OH + NO \quad (3)$$

and all OH radicals are tied up with NO$_2$ in reaction 1 before they reach the OH LIF detection region. Under typical conditions, optimized for the largest IR-induced signal-to-background ratio, the initial mixing ratios are 0.1−0.2% NO$_2$ and 0.04−0.1% H$_2$ at a total helium−nitrogen ballast pressure of 15−25 Torr. A bubbler with an aqueous solution of PNA is used in place of the microwave setup to calibrate the intensity of the near-IR vibrational photodissociation signal against the known photodissociation cross-sections of PNA.[23]

Results and Discussion

Figure 2 displays a photodissociation spectrum observed by detecting OH fluorescence while scanning the frequency of the near-IR excitation laser. The spectrum consists of at least seven partly overlapping bands distributed between 6000 and 7200 cm^{-1}, i.e., in the frequency range characteristic of the first OH stretching overtones. The occurrence of photodissociation at these excitation frequencies implies that the parent molecule is weakly bound ($D_0 < \approx 7000$ cm^{-1}). The signal requires all components of the experiment including the microwave discharge, pump and probe lasers, and H$_2$ and NO$_2$ flows. Adding NO to the mixture to convert possible HO$_2$ photofragments into OH

$$HO_2 + NO \rightarrow OH + NO_2 \quad (4)$$
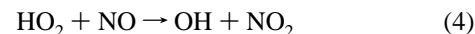
does not affect the signal, indicating that the molecule(s) responsible for the observed spectrum must directly produce OH upon absorption of IR radiation. We explicitly verified that no known stable impurities or secondary reaction products, such as HNO$_3$, HONO, H$_2$O, etc. produce an IR-induced OH signal under comparable conditions (e.g., via a two-photon vibra-

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TABLE 1: Estimated Gas-Phase Band Frequencies (cm^{-1}) of the OH Stretching Vibrations of HOONO Conformers^a

molecule	ν_1(exp) gas^b	ν_1(exp) Ar matrix^b	matrix/gas	ν_1(est) gas	$2\nu_1$(est) gas
cis-cis HOONO		3285		3298	6430
cis-perp HOONO				3554	6940
trans-perp HOONO		3545		3574	6980
HNO$_3$	3550	3521	0.9918		
HO$_2$	3436	3413	0.9933		
t-HONO	3591	3558	0.9908		
c-HONO	3426	3412	0.9959		

^{a} The fractional matrix shifts for the cis-cis (0.9959) and trans-perp (0.9920) HOONO fundamentals are taken as the shift for c-HONO and the average of HNO$_3$, HO$_2$, and t-HONO shifts, respectively. The fundamental frequency of the cis-perp conformer is estimated from that of the trans-perp conformer and the ab initio frequency shift (20 cm^{-1}) between them.[19] Anticipated overtone band centers are obtained from the estimated OH fundamental frequencies using an anharmonicity constant of 83 cm^{-1} (average for OH, HNO$_3$, and HO$_2$NO$_2$). ^{b} References 12, 26, and 28.

TABLE 2: Observed Band Positions (cm^{-1}) in the Overtone Photodissociation Spectrum of HOONO Shown in Figure 2^a

band center (± 15 cm^{-1})	rel intensity	tentative assignment
6180	0.1	
6365	1	$2\nu_1$ (cis-cis)
6505	0.5	$2\nu_1 + \nu_9$ (cis-cis)
6630	0.2	$2\nu_1 + 2\nu_9$ (cis-cis)
6730	0.9	
6935	5^b	$2\nu_1$ (cis-perp & trans-perp)
7045	0.6^b	$2\nu_1 + \nu_9$ (cis-perp & trans-perp)
7155	0.2	$2\nu_1 + 2\nu_9$ (cis-perp & trans-perp)

^{a} The specified band assignment (ν_1 = OH stretch; ν_9 = NOOH torsion) must be regarded as highly tentative. The assignment for the strong band at 6730 cm^{-1} is presently unclear. ^{b} Overlap with each other.

tionally mediated dissociation by the IR pump and UV probe lasers[25]). PNA does photofragment into HO$_2$ and NO$_2$ in this excitation frequency range, but its spectrum, shown in Figure 2 for comparison, is very different from the spectrum observed here. On the basis of the available spectroscopic and theoretical evidence,[10,12,18,19] we argue below that HOONO conformers are the carriers of the bands shown in Figure 2.

In the absence of any data on gas-phase spectroscopy of HOONO,[26] the complete assignment of the observed overtone spectrum is a challenging task. The only existing infrared spectra of HOONO were observed in matrix isolation studies after UV irradiation of HNO$_3$ in solid argon.[10-12] Bands at 3285 and 3545 cm^{-1} were assigned to the OH stretching fundamental vibrations of cis-cis and trans-perp conformers (Figure 1) of HOONO, respectively. The third conformer of HOONO, cis-perp, was not observed in the matrix although it is calculated to have an intermediate stability compared to the other two.[19] Using the available matrix data, combined with typical values for OH matrix shifts and vibrational anharmonicities, the first OH stretching overtones can be estimated as 6430, 6940, and 6980 cm^{-1} for cis-cis, cis-perp, and trans-perp conformers of HOONO, respectively (see Table 1). The estimated overtone positions closely match the positions of the strongest features in the experimental spectrum (Figure 2 and Table 2) suggesting that it arises from photofragmentation of HOONO. Based on our simple analysis, we tentatively assign the band at 6365 cm^{-1} to the $2\nu_1$ transition of the cis-cis conformer, and the anomalously wide 6935 cm^{-1} band to the overlapping $2\nu_1$ transitions of cis-perp and trans-perp isomers. The remaining bands are likely to be combinations of $2\nu_1$ with low-frequency vibrational

modes of HOONO. For example, the bands at 6505 and 6630 cm^{-1} could be combinations of cis-cis $2\nu_1$ with ν_9 and $2\nu_9$, where ν_9 is the NOOH torsional mode. Similarly, the bands at 7045 and 7155 cm^{-1} could be the corresponding combinations for the cis-perp/trans-perp conformers. The NOOH torsional mode is predicted by ab initio calculations to carry a large oscillator strength and, depending on the conformer, have harmonic frequencies of 200–400 cm^{-1}.[18-20,27] Provided that our assignment is correct, the much lower experimental values for ν_9 frequencies (140 cm^{-1} for the cis-cis conformer and 110 cm^{-1} for the -perp ones) would indicate a large degree of structural "floppiness" in HOONO. However, in the absence of more reliable information on HOONO spectroscopy, such assignments should be regarded as highly tentative.

Predicting relative intensities is especially problematic. According to the ab initio calculations of McGrath and Rowland,[19] the relative energies of the three stable conformers of HOONO are 0 (cis-cis), 0.7 (cis-perp), and 2.8 (trans-perp) kcal/mol. The corresponding predicted relative intensities for the OH stretching fundamentals are quite similar (32, 40, and 44 km/mol, respectively). Assuming that the scaling between the overtone and fundamental intensities is the same for all conformers, and using ideal gas thermodynamic properties of HOONO calculated in ref 19, one predicts that the relative $2\nu_1$ intensities at 253 K should be 1.0, 0.45, and 0.008 for the cis-cis, cis-perp, and trans-perp HOONO, respectively. The observed intensity pattern (1.0 for cis-cis and 5.0 for the combination of cis-perp with trans-perp) appears to be disturbingly different from the estimated one. The band intensity for the trans-perp isomer is especially at odds with the predictions considering its quite noticeable contribution to the width of the 6935 cm^{-1} band and also the fact that this conformer was the first to be discovered in the matrix.[12]

The photodissociation spectrum shown in Figure 2 is, however, a convolution of the absorption cross section with the presently unknown dissociation quantum yield. The dissociation energy of the cis-cis conformer of HOONO is calculated to be 6580 cm^{-1},[18] i.e., higher than its presumed $2\nu_1$ band origin (6365 cm^{-1}). The intensity of the cis-cis $2\nu_1$ band may therefore be suppressed relative to the intensities of higher frequency vibrations. The assumption of equal scaling between $2\nu_1$ and ν_1 intensities is also highly questionable, especially when comparing hydrogen-bonded with free OH stretches. In addition, HOONO conformers are known to be separated from each other by sizable barriers,[5,8] possibly preventing complete equilibration among them on the time scale of our experiment. Finally, the exponential sensitivity of the predicted intensities on the relative energies of HOONO conformers makes such predictions less trustworthy. A reexamination of the relative stabilities of HOONO conformers may help to resolve these issues.

From the point of view of atmospheric chemistry, the product branching ratio k_{1b}/k_{1a} is the most interesting quantity. Although we cannot provide a rigorous quantitative measurement of this ratio, we are able to estimate it from relative measurements of PNA vs HOONO photolysis rates under well-characterized conditions. To do this, a known amount of PNA (as measured by FTIR spectroscopy) is admitted in the photolysis chamber and both the photolysis spectrum of PNA and the OH time profile are recorded. The PNA flow is then replaced by the H–NO$_2$ flow and the corresponding data are taken for HOONO under essentially unchanged conditions (the LIF probe laser power is increased by a calibrated amount to account for the weaker signal from HOONO). The concentration of H atoms making it from the microwave discharge region to the mixing
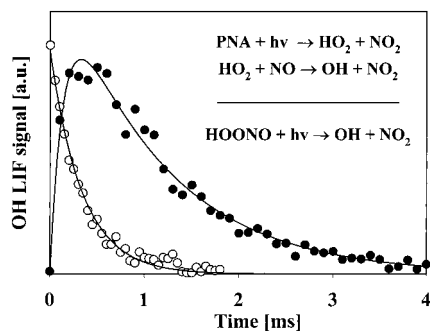
Figure 3. Kinetic traces of OH produced in the infrared photolysis of HOONO (open circles) and PNA (filled circles) as a function of the pump−probe delay. The signals have not been corrected for the difference in probe laser powers. The primary product of PNA photolysis is HO_2, which is converted into OH via reaction with NO. Kinetic data shown here, in conjunction with photolysis spectra of HOONO and PNA taken under well-defined conditions, are used to estimate the product branching ratio in reaction 1.

point is quantified using NO_2 titration, allowing for calculation of the final HNO_3 density. The $[HNO_3]$ and $[NO_2]$ concentrations are additionally verified using FTIR spectroscopy under similar flow conditions and found to agree with the results of titration measurement to within 20%.

Figure 3 shows sample kinetic traces of OH concentrations following the near-IR photolysis of PNA and HOONO. Photolysis of PNA produces HO_2, which is converted into the detected OH via reaction 4 with NO. The rise time of the observed trace is consistent with the rate of reaction 4, and the decay is almost entirely due to the reaction of OH with PNA. Photolysis of HOONO generates OH on the time scale of the pump laser pulse, consistent with OH being the primary photoproduct. The OH decay in this case is mostly due to reaction 1. With this information at hand, the relative initial amounts of HO_2 and OH produced in the photolysis of PNA and HOONO is calculated in a straightforward manner. Assuming that the integrated absorption transition strength is the same for PNA and HOONO overtones and correcting for the nonunity dissociation quantum yield of PNA (0.16 at 253 K),[23] we can estimate the density of HOONO in the photolysis chamber.

We estimate, using the method described above, that $[HOONO]/[HONO_2] = 0.05 \pm 0.03$ at 253 K in 20 Torr helium−nitrogen buffer approximately 0.3 s after the mixing of OH and NO_2. The uncertainties do not include systematic errors due to the assumptions described above, some of which are not fully substantiated. For example, HOONO dissociation quantum yield of less than 1 would tend to increase the ratio. On the other hand, our inclusion of the HOONO combination bands in the integrated signal decreases the ratio somewhat. The integrated absorption cross sections for HOONO and PNA are likely to be different, but probably not by more than 50%. But even combining all these uncertainties together, we do not expect the actual ratio to be off by more than a factor of 2. Thus, the results presented here imply an approximate lower limit of $5 \pm 3\%$ for the branching ratio k_{1b}/k_{1a}.

Our result is marginally consistent with the upper limit for HOONO yield obtained by Burkholder et al. (5%)[9] but overlaps well with the upper limit from the work of Dransfield et al. (10%).[8] The isotope-specific kinetics study of reaction 1 by Donahue et al.[5] and calculations by Golden and Smith[4] appear to be on a higher side of the ratio reported here. However, one has to be careful when comparing different experiments with each other, as the yield of HOONO is likely to depend strongly

on experimental conditions. In addition, the unimolecular lifetime of HOONO has to be quantified before the $[HOONO]/[HNO_3]$ ratio obtained here for a fixed time delay (0.3 s) between mixing and observation can be related to the actual branching ratio k_{1b}/k_{1a}. We are presently in a process of modifying our apparatus to make it suitable for flow tube kinetics experiments, both to put the preliminary measurements described here on a more quantitative basis and to investigate the chemistry of HOONO in more detail.

In summary, this Letter presents the first observation of a gas-phase spectrum of HOONO, a structural isomer of nitric acid that has long eluded experimentalists. Although a complete vibrational analysis of the spectrum is not feasible at the present time, both the number of the observed bands and their positions are consistent with the available spectroscopic information on this molecule. We have shown that the fraction of HOONO produced in the association reaction of OH with NO_2 is relatively small, of the order of a few percent. It remains to be seen whether this product channel becomes more significant at lower temperatures and higher pressures. From an experimental kinetics perspective, the successful observation of HOONO by photodissociation spectroscopy under ambient temperature conditions opens the door to many interesting experiments on reactions involving weakly bound adducts such as, for example, ROONO and RO_2-H_2O (R = organic radical).

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