Aqueous Peroxynitric Acid ($HOONO_2$): A Novel Synthesis and Some Chemical and Spectroscopic Properties

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Peroxynitric acid, $HOONO_2$, can be prepared in aqueous solution by the reaction of nitrous acid with a greater-than-2-fold excess of hydrogen peroxide at or below 0 °C. Under optimum conditions, concentrations in excess of 1.5 M can be obtained. In acid solution at room temperature, the compound has a ca. 30 min half-life for decomposition; in alkaline solution, decomposition is very rapid, yielding nitrite ion and oxygen. The aqueous acid is a potent oxidizing agent, reacting rapidly with I^-, Br^-, Cl^-, N_3^-, and VO^{2+}. Raman, UV, and ^{15}N NMR spectra of the aqueous acid have been obtained. The Raman spectra reveal three new fundamental vibrations of the peroxynitric acid molecule, leaving only two that have yet to be positively identified. The UV spectrum shows a monotonic rise in absorbance between 290 and 230 nm; the ^{15}N NMR resonance has a chemical shift of −28.3 ppm relative to dilute nitric acid.

Introduction

Although the earliest reports of peroxynitric acid, $HOONO_2$, date back to the work of D'Ans and Friederich[1] and the subsequent study by Schwarz,[2] convincing characterization of the compound was only obtained in relatively recent times after its photochemical synthesis in the vapor phase by the combination of NO_2 with HO_2.[3] A more practical synthetic method was subsequently developed by Kenley et al.,[4] consisting of reaction of NO_2BF_4 with 90% hydrogen peroxide, followed by transfer of the peroxynitric acid out of the reaction solution in a stream of argon. This permitted the preparation and investigation of relatively pure dilute aqueous solutions of the acid. In the meanwhile, peroxynitric acid has been detected in Earth's atmosphere,[5,6] and considerable interest has arisen in the role that it may play in atmospheric photochemistry.

We recently became interested in the oxidizing properties of the $HNO_2-H_2O_2$ system, which is known to involve the transient formation of peroxynitrous acid, HOONO.[7] While examining the behavior of this system, we observed that when a substantial excess of hydrogen peroxide was present, a powerfully oxidizing species persisted long after the HOONO would have decayed away. We were able to convince ourselves that this species was, in fact, peroxynitric acid, and optimization of the rather simple synthesis led to the preparation of solutions in excess of 1.5 M. At such concentrations, a wide variety of chemical and physical measurements on peroxynitric acid become feasible. In particular, it has become practical for the first time to measure the compound's Raman spectrum.

Experimental Section

Synthesis of Peroxynitric Acid Solutions. Peroxynitric acid solutions were prepared by the reaction of sodium nitrite with a substantial excess of hydrogen peroxide in aqueous acid. The nitrite solution must be added gradually to the cooled and acidified hydrogen peroxide, which should be present in well over 2-fold excess. (As the ratio $[H_2O_2]:[NO_2^-]$ is reduced to near 2:1, substantial gas evolution is observed, and the yield of peroxynitric acid drops precipitously.) Enough acid must be present to protonate all or nearly all of the nitrite ion, and the reaction temperature should be held at or below 0 °C. A moderately optimized procedure is the following:

In 1.5 cm^3 (15 mmol) of 30% H_2O_2 is dissolved 0.53 g (7.5 mmol) 98% $NaNO_2$, and the solution is cooled in an ice bath. Another 1 cm^3 (10 mmol) of 30% H_2O_2 is mixed with 0.15 cm^3 (1.7 mmol) 70% $HClO_4$ in a vial with a Teflon-coated magnetic stirring bar, and the mixture is cooled to −20 °C in an alcohol bath on a stirring thermoelectric "cold plate." The nitrite−peroxide solution is added to the stirred peroxide−acid solution from a syringe in 0.01 cm^3 increments. After each 0.25 cm^3 addition of nitrite−peroxide solution, a further 0.1 cm^3 of 70% $HClO_4$ is added, for a total of 0.65 cm^3 (7.3 mmol) of acid, followed by the balance of the nitrite−peroxide solution. The resulting product solution (about 3.3 cm^3) will typically be approximately 1.7 M in peroxynitric acid, corresponding to a 75% yield based on sodium nitrite taken. The solution will also be about 3.3 M in hydrogen peroxide. Peroxynitric acid solutions intended for Raman spectrometry were made similarly, except that the perchloric acid was replaced by the same number of moles of 70% nitric acid in order to minimize the number of extraneous polyatomic species present in the solution.

Analytical Procedures. For routine determination of peroxynitric acid concentrations, an acidified 0.1 M solution of KI was cooled in an ice bath, and a sample of the peroxynitric acid solution was added. The liberated I_3^- was titrated immediately with standard thiosulfate solution, and the gradually drifting end point, which results from the slow reaction of hydrogen peroxide with iodide ion, was followed with time and extrapolated back to the time of mixing to give the peroxynitric acid titer. The total oxidizing power of the solution ($HOONO_2 + H_2O_2$) was determined by adding a sample to acidified 0.2 M KI at room temperature, followed by addition of a small amount of ammonium molybdate to catalyze reaction of H_2O_2 with I^- and finally by titration with thiosulfate.[8]

In order to determine the amount of nitrite ion produced in the alkaline decomposition of peroxynitric acid, the excess peroxide was

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first titrated potentiometrically with 10% sodium hypochlorite.[9] The nitrite was then allowed to react with an excess of potassium permanganate in sulfuric acid, the excess of permanganate was reduced with iodide, and the liberated iodine was titrated with thiosulfate.[8]

In order to determine the amount of oxygen liberated in the alkaline decomposition of peroxynitric acid, a sample of the acid was placed in one leg of a two-legged reaction vessel, and an excess of sodium hydroxide solution was placed in the other. Both solutions were frozen, and the vessel was closed and evacuated through an attached stopcock. The solutions were then thawed and mixed, and the evolved gas was quantified by taking successive "heads" into a large standardized volume and measuring the pressure with a Baratron capacitance manometer. Measurement with a quadrupole mass spectrometer confirmed that the gas was essentially all oxygen.

Ultraviolet Spectrometry. Ultraviolet spectra were determined at 15−20 °C in rectangular silica cells of 1-cm light path in a Hewlett Packard Model 8452A diode array spectrometer with 2 nm resolution. Data were subjected to three-point smoothing. Measurements were completed in less than 1 min, and correction was made for the small amount of peroxynitric acid decay that took place during this time. The spectrum of each solution was remeasured after all of the peroxynitric acid had decomposed, and the difference between the two spectra, divided by the peroxynitric acid concentration at the time of the initial measurement, gave apparent extinction coefficients, ϵ_{app}, which could be related to the true extinction coefficients of peroxynitric acid, ϵ_{HNO_4}, by the relation

$$\epsilon_{app} = \epsilon_{HNO_4} - n_{NO_3^-}\epsilon_{NO_3^-} + n_{H_2O_2}\epsilon_{H_2O_2}$$

where $\epsilon_{NO_3^-}$ and $\epsilon_{H_2O_2}$ are the respective extinction coefficients of nitrate ion and hydrogen peroxide, and $n_{NO_3^-}$ and $n_{H_2O_2}$ are respectively the number of moles of nitric acid produced and the number of moles of hydrogen peroxide consumed in the decay of 1 mol of peroxynitric acid. Values of ϵ_{HNO_4} were calculated using directly measured values of $\epsilon_{NO_3^-}$ and $\epsilon_{H_2O_2}$ along with values of 1 and 0.7 for $n_{NO_3^-}$ and $n_{H_2O_2}$, respectively. (The value of $n_{H_2O_2}$ is based on results detailed later in this paper.) The spectra of the solutions resulting from the decay of the peroxynitric acid were quantitatively consistent with the values of n and ϵ and with the initial concentrations of $HOONO_2$ and H_2O_2.

NMR Spectrometry. Samples of peroxynitric acid for ^{15}N NMR spectrometry were made using sodium ^{15}N nitrite (Isotec) and were diluted with D_2O. Measurements were made at a Larmor frequency of 30.452 MHz with a GE gn-based Model 293 Omega spectrometer (7.06 T). Spectra were recorded with 24 kHz spectral width, 9 μs (70°) pulse width, 5.44 s acquisition time, and 40 s repetition interval. Data sets consisting of 128 000 points were collected. Chemical shifts are reported with respect to internal nitric acid (ca. 0.25 M).

Raman Spectrometry. Samples for Raman spectrometry were contained in a glass tube sealed into and protruding through the bottom of a Dewar-type cooling jacket. The design is similar to that described by Strommen and Nakamoto.[10] The jacket was filled with an ice−salt mixture at about −18 °C, and the sample itself was probably no warmer than 0 °C. Samples were excited with the 514.5 nm line of an argon ion laser (Spectra Physics Model 165), and Raman-scattered light was collected using a 90° scattering geometry. The Raman spectrometer consisted of a triple monochromator (Spex Model 1877D) with *f*/0.95 collection optics (D. O. Industries). A liquid-nitrogen-cooled CCD camera (Photometrics Model CH210) was used for detection of the Raman signal. Depolarization measurements were made by placing a polarization analyzer immediately after the collection optics and a polarization scrambler in front of the entrance slit of the monochromator (Method VII of Claassen et al.[11]). Spectra were recorded in five regions, typically using 100 mW excitation and 100−200 s signal integration. Each spectral region was calibrated to ±1 cm^{-1} against the emission lines of an appropriate low-pressure discharge lamp. Spectra of solutions of hydrogen peroxide in nitric acid were measured and compared with the spectra of the peroxynitric acid solutions in order to permit elimination of those bands that were not attributable to the peroxynitric acid molecule.

Results

Analytical Verification of the Nature of the Oxidant. The iodometric method used to analyze for peroxynitric acid merely confirms the existence of a strong oxidant. By itself it establishes neither the nature of the oxidizing species nor the number of moles formed. To verify the nature of the oxidant and validate the analytical procedure, we have related the iodometric titer (extrapolated back to the time of addition of iodide; see Experimental Section) to the production of nitrite ion and oxygen when the oxidant solution is made alkaline. An oxidant solution with a prompt iodometric titer of 3.02 ± 0.08 mequiv/cm^3 reacted with excess base to produce 1.50 ± 0.09 M nitrite. Another solution with a prompt iodometric titer of 3.20 ± 0.07 mequiv/cm^3 reacted with excess base to evolve 1.59 ± 0.05 mmol of O_2/cm^3. These results are consistent with the reactions

$$HOONO_2 + 2H^+ + 3I^- \rightarrow H^+ + NO_3^- + I_3^- + H_2O \quad (1)$$

$$HOONO_2 + OH^- \rightarrow NO_2^- + O_2 + H_2O \quad (2)$$

General Observations. In dilute acid solution (pH 1−2), peroxynitric acid decomposes with a half-life of about 30 min at ca. 22 °C. In a typical experiment, a solution 0.0745 M in $HOONO_2$ and 0.1572 M in H_2O_2 was allowed to decay. After the peroxynitric acid was completely gone, 0.1094 M hydrogen peroxide remained, corresponding to the consumption of 0.64 mol of H_2O_2/mol of peroxynitric acid.

We have already noted the rapid reaction of peroxynitric acid with base and with iodide, and we have confirmed the rapid oxidation of bromide that has been noted by others.[1,2,12] In addition, we find that peroxynitric acid rapidly oxidizes chloride, azide, and 4-valent vanadium. Divalent copper brings about a vigorous reaction, apparently consisting of catalytic decomposition of the peroxyacid. Stirring a peroxynitric acid solution with benzene leads to gradual development of a yellow color. Analysis by gas chromatography−mass spectrometry indicates the formation of mono- and dinitrobenzenes, nitrophenol, and quinone.

We attempted to distill peroxynitric acid from aqueous solution in an argon stream, following the method used by Kenley et al. to transfer the compound from 90% H_2O_2.[4] Neither mass spectrometry nor IR spectrometry gave indication of any significant product in the gas phase. Apparently the compound is not significantly volatile from relatively dilute aqueous solution.

Spectrometric Results. Our data for the UV spectrum of peroxynitric acid in 0.01 M $HClO_4$ between 230 and 290 nm are summarized in Table 1. Also given in the table are the values of ϵ_{HNO_4} obtained in a pulse radiolysis study by Løgager and Sehested.[13]

Peroxynitric acid was found to have a sharp ^{15}N NMR resonance ($\Delta\nu_{1/2}$ ca. 0.6 Hz) with a chemical shift of −28.3 ppm referenced to internal ca. 0.25 M nitric acid (i.e., at lower frequency than the reference). This is in the same region as shifts that have been observed in strongly acidic nitrous acid solutions and that have been attributed to the NO^+ cation.[14]

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Table 1. Ultraviolet Extinction Coefficients of Peroxynitric Acid[a]

wavelength (nm)	ϵ_{app}[b]	$\epsilon_{H_2O_2}$[b]	$\epsilon_{NO_3^-}$[b]	ϵ_{HNO_4}[b]	ϵ_{HNO_4}[c]
230	−444	66	940	450	
240	163	41	122	256	400[d]
250	155	24.8	11.6	149	230
260	96	14.4	1.7	88	150
270	53	7.9	1.9	49	90
280	21.5	4.2	3.5	22	35
290	4.5	2.3	5.5	8.4	

[a] All extinction coefficients in units of M^{-1} cm^{-1}. [b] This work in 0.01 M $HClO_4$. Measurements were made in cells of 1 cm light path with concentrations adjusted so that the measured optical densities lay between 0.1 and 0.9. $\epsilon_{app} = [(OD)_{initial} - (OD)_{final}]/[HOONO_2]_{initial}$. Extinction coefficient of peroxynitric acid = $\epsilon_{HNO_4} = \epsilon_{app} + \epsilon_{NO_3^-} - 0.7\epsilon_{H_2O_2}$ (for details see text). We estimate the limits of error in ϵ_{HNO_4} to be ±20% at 230 nm and ±10% at all other wavelengths. [c] Reference 13; in 0.01 M HNO_3. [d] Maximum.

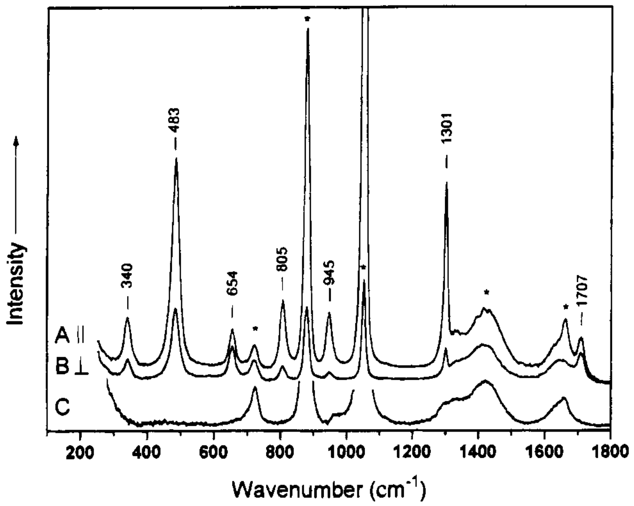

Figure 1. Raman spectra of aqueous peroxynitric acid and of an aqueous HNO_3/H_2O_2 reference solution. Spectra A and B are of a solution ca. 1.6 M in $HOONO_2$, 3 M in HNO_3, and 3 M in H_2O_2. They are taken with the polarization of the scattered light parallel and perpendicular, respectively, to that of the exciting light. Spectrum C is of a reference solution approximately 3 M each in HNO_3 and H_2O_2. Bands common to the sample and reference spectra are marked with an asterisk. Frequencies are indicated only for those bands that are unique to $HOONO_2$.

In Figure 1 is displayed the Raman spectrum of an aqueous peroxynitric acid solution measured with parallel and perpendicular polarizations. Also shown is the spectrum of a reference solution that is about 3 M each in nitric acid and hydrogen peroxide. The peroxynitric acid Raman bands are listed in Table 2, along with the bands observed for gaseous peroxynitric acid by infrared and microwave spectroscopy.[3,15,16] For comparison, we have also tabulated the corresponding bands of the isoelectronic compound "fluorine nitrate," $FONO_2$.[17,18] The tentative band assignments are based primarily on analogy with $FONO_2$.[18]

Discussion

Our analytical results and the agreement of our Raman spectrum with published infrared data leave little doubt that we have in fact prepared peroxynitric acid in aqueous solution. The formation of this compound from nitrous acid and hydrogen peroxide is certainly unexpected, and we can only speculate as to the mechanism involved. A sequence of reactions that is at least plausible is

$$HNO_2 + H_2O_2 \rightarrow HOONO + H_2O \qquad (3)$$

$$HOONO \rightleftharpoons OH + NO_2 \qquad (4)$$

$$OH + H_2O_2 \rightarrow HO_2 + H_2O \qquad (5)$$

$$NO_2 + HO_2 \rightleftharpoons HOONO_2 \qquad (6)$$

which would be competing with reactions such as

$$HOONO \rightarrow H^+ + NO_3^- \qquad (7)$$

$$OH + HNO_2 \rightarrow NO_2 + H_2O \qquad (8)$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \qquad (9)$$

$$2NO_2 + H_2O \rightarrow HNO_2 + H^+ + NO_3^- \qquad (10)$$

In a recent paper, Koppenol et al.[19] questioned whether reaction 4 is really involved in the decomposition of HOONO. They have suggested that decomposition of peroxynitrous acid at high acidity takes place by way of the reaction

$$HOONO + H^+ \rightarrow NO_2^+ + H_2O \qquad (11)$$

If this is true, an alternative mechanism for the formation of peroxynitric acid in our system might be reactions 3 and 11, followed by

$$NO_2^+ + H_2O_2 \rightarrow HOONO_2 + H^+ \qquad (12)$$

Reaction 12 is presumably the one responsible for the formation of peroxynitric acid in the interaction of concentrated hydrogen peroxide with N_2O_5, concentrated HNO_3, and NO_2BF_4.[1,2,4]

In alkaline solution, the decomposition of peroxynitric acid is generally accepted to proceed by reaction 2.[4,12,13] The situation in acid is less clear. Løgager and Sehested[13] have suggested the simple acid equivalent of reaction 2:

$$HOONO_2 \rightarrow HNO_2 + O_2 \qquad (13)$$

followed by

$$HOONO_2 + HNO_2 \rightarrow 2H^+ + 2NO_3^- \qquad (14)$$

and, if hydrogen peroxide is present, by reactions 3 and 7, with reaction 3 proceeding at about 3 times the rate of reaction 14. Lammel et al.,[12] on the other hand, have suggested that the decomposition in acid takes place via the reverse of reaction 6, followed by reactions 9 and 10. Their mechanism appears to be incomplete, however, since they do not consider reactions 3 and 14. And involvement of reactions 4 and 5 would add further complications. Løgager and Sehested find that, in acid solutions containing excess H_2O_2, 1 mol of H_2O_2 is consumed for each mole of $HOONO_2$ that decays, which supports their conclusion that in such solutions the decomposition of $HOONO_2$ proceeds by way of reactions 13, 3, and 7. We observe the ratio $\Delta[H_2O_2]/\Delta[HOONO_2]$ in such solutions to be 0.64, which suggests a somewhat more complicated decomposition mecha-

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Table 2. Molecular Vibrational Bands (cm^{-1}) of Peroxynitric Acid and Analogous Bands of Fluorine Nitrate[a]

	$HOONO_2$		$FONO_2$[e]	
mode (in $HOONO_2$)[b]	IR (g)[c]	Raman (aq)[d]	IR (g)	Raman (l)
$O-NO_2$ torsion	(145)[f]		152 vvw	165 vw, dp
O−H torsion				
N−O−OH bend		340 mw, p	303 vw	304 m, p
N−OOH str		483 s, p	454 ms[g]	457 s, p[g]
$O-NO_2$ in-plane def		654 mw, dp	633 m	636 m, dp
$O-NO_2$ out-of-plane def	722 (?) vw[h]		708 m	708 vvw, p
NO_2 scissor	802.7 m	805 m, p	804 s[g]	800 m, p[g]
?	919.2 vw			
?	922.1 vw			
O−O str	941.0 w	945 m, p	928 m	929 s, p
NO_2 sym str	1303.9 m	1301 s, p	1301 vs	1302 s, p
O−O−H bend	1396.5 mw			
NO_2 asym str	1728.3 s	1707 mw, dp	1759 vs	1760 vw, dp
O−H str	3540.1 w			

[a] Abbreviations: s = strong, m = medium, w = weak, v = very, p = polarized, dp = depolarized. [b] Tentative assignment and approximate description. [c] Unless otherwise noted, from ref 3 (without assignments). [d] This work. Frequencies accurate to ± 2 cm^{-1}. [e] Reference 18. [f] From microwave spectrum; ref 15. [g] The authors of ref 17 have interchanged these two assignments. [h] From ref 16 (without assignment).

nism. (For the interpretation of our UV spectra of peroxynitric acid, we have compromised on an intermediate value of 0.7 for this ratio.)

The rate of decomposition that we observe for peroxynitric acid in dilute acid is nearly a factor of 2 less than that observed by Løgager and Sehested,[13] which, in turn, is less than half that reported by Kenley et al.[4] It should perhaps not be too surprising that it has not been possible to obtain consistent results for the rate of a rather slow decomposition involving free-radical intermediates.

Prior to our present work, the UV spectrum of aqueous peroxynitric acid has not been extensively studied. Jesson et al.[20] reported the spectrum of a concentrated HNO_3/H_2O_2 mixture between 300 and 360 nm, but the only measurements that are directly comparable to ours are to be found in the recent pulse-radiolysis study by Løgager and Sehested.[13] Our UV extinction coefficients for $HOONO_2$ are only about 60% of the magnitude of those reported in the latter work. We do not know the reason for this discrepancy, but we feel fairly confident of our quantitation. Løgager and Sehested also observe a maximum in the spectrum at 240 nm, whereas our spectrum continues to rise monotonically at least to 230 nm. Again we are not sure of the reason for the discrepancy. We note, however, that Løgager and Sehested made most of their measurements in 0.01 M nitric acid, which is rather opaque at 240 nm and below. Hence small errors in nulling out the reference spectrum could lead to spurious results. We may also note that the UV absorption cross sections for gaseous $HOONO_2$ rise to more than 6000 M^{-1} cm^{-1} at 190 nm and show no maximum at longer wavelength.[21,22] Løgager and Sehested also show the spectrum of the $OONO_2^-$ ion at pH 9.7, which is shifted to longer wavelength with $\epsilon_{max} = 1600$ M^{-1} cm^{-1} at about 280 nm.[13]

In our Raman spectra we have identified three more of the twelve fundamental vibrations of the peroxynitric acid molecule and have obtained qualitative polarization data for seven of these bands. The data presented in Table 2 indicate that the vibrational spectrum of $HOONO_2$ can be correlated quite well with that of the isolectronic compound "fluorine nitrate", $FONO_2$,[17,18,23,24] and we have made tentative assignments of the peroxynitric acid vibrations by analogy with those of $FONO_2$, along with the bending and stretching bands associated uniquely with the OH group of $HOONO_2$. We see that all but two of the expected fundamentals of peroxynitric acid have now been positively identified. The O−O−H torsion band, predicted by theory to lie between 200 and 300 cm^{-1},[25,26] remains undetected, while the assignment of the $O-NO_2$ out-of-plane deformation is open to question. We may expect both of these bands to be quite weak, and in our Raman experiment the latter one may very well lie under the nitrate bending vibration at 721 cm^{-1}. The O−O−H bending mode of $HOONO_2$, which is seen as a medium-weak band in the IR, is expected to be very weak in the Raman and is probably concealed under the corresponding band of H_2O_2 and the asymmetric stretch of NO_3^- around 1400 cm^{-1}. (Compare with the spectra of peroxymonosulfate, $HOOSO_3^-$.[27]) And we may expect the O−H stretch of peroxynitric acid to be similarly buried in the Raman under the corresponding broad bands of solvent and hydrogen peroxide around 3500 cm^{-1}. We have also been unable to detect the weak low-frequency $O-NO_2$ torsion band, which has been seen in the microwave spectrum.[15]

The Raman spectra of gaseous and liquid $FONO_2$ have been interpreted in terms of a molecule with C_s symmetry, in which the FO moiety lies in a plane that bisects the NO_2 group and is perpendicular to the O_2NO plane.[17,18] This structure is derived from the observation of broad, depolarized bands in the Raman spectrum, particularly the band assigned to the asymmetric NO_2 stretch, and the assignment of these bands to species A″. Such an argument is treacherous, however, since in molecules of low symmetry the A or A′ modes will generally have nondiagonal polarizability components, and some of these bands may be depolarized or only very weakly polarized.[28] More recent results, in fact, indicate that the $FONO_2$ molecule is almost

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certainly planar,[24,29] as are its heavier homologs $ClONO_2$ and $BrONO_2$.[30] It therefore appears that Raman depolarization data are incapable of providing definitive structural information for molecules of such low symmetry. In the case of peroxynitric acid, the microwave spectrum has been interpreted to indicate that the heavy atoms lie in a plane, with the hydrogen atom above or below this plane.[15] Theoretical calculations have led to a generally similar structure, except that they have indicated a dihedral angle of 23.9° between the plane of the peroxy oxygens and that of the NO_2 moiety.[26] This difference very probably lies within the limits of accuracy of the theoretical calculations.

Conclusions

We have developed a facile synthetic method for the production of high concentrations of peroxynitric acid in aqueous solution. This has permitted us to obtain the Raman spectrum of the aqueous acid and thereby to identify three new vibrational bands of the molecule. We anticipate that the availability of this straightforward synthetic procedure will open the door to extensive future investigation and application of the reaction chemistry of this potent oxidizing species and may perhaps lead to new insights into its behavior in Earth's atmosphere.

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