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Novel Onium Salts. Synthesis and Characterization of the Peroxonium Cation, H_2OOH^+

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The synthesis and properties of $H_3O_2^+Sb_2F_{11}^-$, $H_3O_2^+SbF_6^-$, and $H_3O_2^+AsF_6^-$, the first known examples of peroxonium salts, are reported. These salts were prepared by protonation of H_2O_2 in anhydrous HF solutions of the corresponding Lewis acids. They were isolated as metastable solids which underwent decomposition to the corresponding H_3O^+ salts and O_2 in the temperature range 20–50 °C. The $H_3O_2^+$ salts were characterized by vibrational and NMR spectroscopy. Modified valence force fields were computed for the isoelectronic series H_2OOH^+, H_2NOH, and H_2NNH^-. The similarity of their observed spectra and computed force fields suggests that the ions are isostructural with H_2NOH which possesses C_s symmetry with the unique hydrogen being trans to the other two hydrogens. The influence of protonation on the stretching frequency of the two central atoms is discussed for the series HOO^-, HOOH, H_2OOH^+, H_2NNH^-, H_2NNH_2, $H_3NNH_2^+$, and $H_3NNH_3^{2+}$. Attempts to protonate both oxygen atoms in H_2O_2 to form $H_4O_2^{2+}(SbF_6^-)_2$ resulted in $H_3O_2^+Sb_2F_{11}^-$ as the only product. The strongly oxidizing Lewis acid BiF_5 underwent a redox reaction with H_2O_2 in HF, resulting in quantitative reduction of BiF_5 to BiF_3, accompanied by O_2 evolution. When a 2:1 excess of BiF_5 was used, an adduct formed having the approximate composition $BiF_3 \cdot BiF_5$. Heating a mixture of solid $H_3O_2^+Sb_2F_{11}^-$ with a strongly fluorinating agent, such as BiF_5 or Cs_2NiF_6, resulted in a green chemiluminescence band centered at 5150 Å.

Introduction

Anhydrous HF–Lewis acid solutions are ideally suited to protonate less acidic substrates. This technique has successfully been applied to the isolation of novel salts containing the H_3O^+,[1-4] H_3S^+,[5,6] $NH_2F_2^+$,[7] and AsH_4^+ [6] cations. Since all these cations contain a single central atom, it appeared interesting to extend this method to a substrate containing two central atoms, such as H_2O_2. In such a case, both single and double protonation are possible, and the influence of protonation on the strength of the bond between the two central atoms can be studied. Such effects are well-known[8] for the related hydrazine molecule. Although the HO_2^- anion is known,[9,10] to our knowledge the corresponding cations derived from H_2O_2 have only been postulated,[11] but not characterized or isolated as salts.

Further interest was added to this study by the fact that H_2O_2 is a starting material for the generation of excited molecular oxygen which in turn is of great interest for a near resonant energy-transfer iodine laser. Therefore, the combination of an $H_3O_2^+$ cation with a strongly oxidizing anion in the form of a stable salt could provide a suitable solid-propellant gas generator for excited oxygen.

Experimental Section

Materials and Apparatus. Volatile materials used in this work were manipulated in well-passivated (with ClF_3 and HF) vacuum lines constructed either entirely from Monel Teflon-FEP or entirely from Teflon-PFA with injection-molded fittings and valves (Fluoroware Inc.). Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. Hydrogen fluoride was dried by treatment with F_2, followed by storage over BiF_5 to remove last traces of H_2O.[3] Antimony pentafluoride and AsF_5 (Ozark Mahoning Co.) were purified by distillation and fractional condensation, respectively. Bismuth pentafluoride (Ozark Mahoning Co.) was used as received. Hydrogen peroxide (90%, FMC Corp.) was purified by repeated fractional crystallization,[12] and material of 99.95% purity, as analyzed by titration with $KMnO_4$ solution, was obtainable by this method. All equipment, used for handling H_2O_2, was washed with 12 N H_2SO_4, thoroughly rinsed with distilled H_2O and dried in an oven prior to use. For the hazards and necessary precautions of handling concentrated H_2O_2 see ref 12. The synthesis of Cs_2NiF_6 has previously been described.[13]

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of dry powders at room temperature were obtained by using pressed (Wilks minipellet press) disks between AgCl windows. Low-temperature spectra were obtained as dry powders between CsI plates with a technique similar to one previously reported.[14]

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[15] for the elimination of plasma lines. Sealed quartz or Teflon-FEP tubes were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature spectra were recorded with a previously described[16] device. Polarization measurements were carried out according to method VIII listed by Claassen et al.[15]

Debye–Scherrer powder patterns were taken with a GE Model XRD-6 diffractometer. Samples were sealed in quartz capillaries (~0.5-mm o.d.).

The ^{19}F and ^1H NMR spectra were recorded at 84.6 and 90 MHz, respectively, on a Varian Model EM 390 spectrometer equipped with a variable-temperature probe. Chemical shifts were determined relative to external $CFCl_3$ and Me_4Si, respectively.

A Perkin-Elmer differential scanning calorimeter, Model DSC-1B, was used for the determination of the thermal stability of the compounds. The samples were sealed in aluminum pans, and heating rates of 2.5 and 10°/min were used.

For the chemiluminescence experiments, $H_3O_2Sb_2F_{11}$ was mixed with either solid BiF_5 or Cs_2NiF_6 and placed into the bottom of a Pyrex glass tube which was equipped with a stopcock. The tube was connected to a vacuum manifold and heated in a dynamic vacuum by a stream of hot air until gas evolution and chemiluminescence were observed. The emitted light was analyzed with a 0.5-m McKee-Pederson monochromator over the range 2000–10 000 Å using a spectral slit width of 25 Å.

Preparation of $H_3O_2^+AsF_6^-$. In a typical experiment, AsF_5 (15.39 mmol) and anhydrous HF (50.76 mmol) were combined at −196 °C is a passivated Teflon-FEP ampule equipped with a valve. The mixture was allowed to melt and homogenize. The ampule was then taken to the drybox, and H_2O_2 of 99.95% purity (15.29 mmol) was syringed in at −196 °C. The ampule was transferred back to the vacuum line and evacuated at −196 °C; it was then kept at −78 °C for 2 days to allow reaction. After this period, no evidence was found for material noncondensable at −196 °C, i.e., no O_2 evolution. The mixture was warmed to −45 °C, and a clear solution resulted. Material volatile at −45 °C was removed by pumping for 10 h and was collected at −196 °C. A white solid residue resulted which was of marginal stability at ambient temperature. On the basis of the observed material balance (weight of 15.29 mmol $H_3O_2AsF_6$: calcd, 3.423 g; found, 3.47 g), the conversion of H_2O_2 to $H_3O_2AsF_6$ was complete within experimental error. The compound was shown by infrared and Raman spectroscopy to contain the $H_3O_2^+$ cation and AsF_6^- anion.[1,7,17-20]

Thermal Decomposition of $H_3O_2^+AsF_6^-$. A sample of $H_3O_2AsF_6$ (28.93 mmol) was allowed to decompose at ambient temperature. An exothermic reaction occurred, generating 14.6 mmol of O_2 and a white solid residue which was identified by vibrational spectroscopy as $H_3O^+AsF_6^-$.[1]

Preparation of $H_3O_2^+SbF_6^-$. Antimony pentafluoride (27.96 mmol) was added in the drybox to a passivated Teflon-FEP U-tube equipped with two valves and a Teflon-coated magnetic stirring bar. Anhydrous HF (522.9 mmol) was added on the vacuum line at −196 °C, and the mixture was homogenized by stirring at 20 °C. In the drybox hydrogen peroxide (27.97 mmol) was syringed into the U-tube at −196

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°C. The cold tube was transferred back to the vacuum line and was evacuated. The tube was warmed from −196 to −78 °C for 1 h with agitation which resulted in the formation of a finely divided white solid, suspended in the liquid HF. When the mixture was warmed to 20 °C, the white solid completely dissolved. No gas evolution was observed during the entire warm-up operation, and no noncondensable material could be detected when the mixture was cooled again to −196 °C. The HF solvent was pumped off at −22 °C for 3 h resulting in 7.566 g of a white solid (weight calculated for 27.96 mmol of $H_3O_2SbF_6$ = 7.570 g), stable at 20 °C. The compound was shown by vibrational spectroscopy to be composed of $H_3O_2^+$ cations and SbF_6^- anions.[1,5,7,18,19] Additional support for the composition of the product was obtained by allowing a sample of $H_3O_2SbF_6$ to thermally decompose at about 45 °C. This decomposition produced O_2 and the known H_3OSbF_6 salt[1] in almost quantitative yield.

Preparation of $H_3O_2Sb_2F_{11}$. The synthesis of this compound was carried out in a manner identical with that described above for the preparation of $H_3O_2SbF_6$, except for using an excess of SbF_5. Thus, the combination of SbF_5 (14.83 mmol), HF (407 mmol), and H_2O_2 (6.83 mmol) produced 3.581 g of a white solid (weight calculated for 6.83 mmol of $H_3O_2SbF_6 \cdot 1.17SbF_5$ = 3.581 g), stable up to about 50 °C. The compound was shown by vibrational and NMR spectroscopy to contain the $H_3O_2^+$ cation and $Sb_2F_{11}^-$ as the principal anion.

The H_2O_2–HF–BiF_5 System. Bismuth pentafluoride (10.68 mmol), HF (394 mmol), and H_2O_2 (10.15 mmol) were combined in a passivated Teflon ampule in a manner analogous to that described for the preparation of $H_3O_2SbF_6$. The mixture was warmed from −196 °C to ambient temperature. During the warm-up operation gas evolution was observed which was accompanied by the formation of a copious white precipitate which showed little solubility in HF at ambient temperature. Bands due to either BiF_6^{-3} or BiF_5[21,22] (both are strong Raman scatterers) could not be detected in the Raman spectra of either the liquid or the solid phase. The evolved gas was removed from the ampule at −196 °C and consisted of 10.1 mmol of O_2. The material volatile at 20 °C was pumped off, leaving behind 2.897 g of a white solid which was identified by vibrational spectroscopy as BiF_3[3,23] (weight calculated for 10.68 mmol BiF_3 = 2.841 g).

When BiF_5 and H_2O_2 in a mole ratio of 2:1 were combined in a similar manner in anhydrous HF solution, the weight of the resulting white stable solid product closely corresponded to that expected for $BiF_3 \cdot BiF_5$. The product was characterized by vibrational spectroscopy which showed it to be an adduct and not a simple physical mixture of BiF_3 and BiF_5.

Results and Discussion

Synthesis. On the basis of the observed material balances, H_2O_2 is protonated in HF–MF_5 (M = As, Sb) solutions according to

$$H_2O_2 + HF + MF_5 \rightarrow H_3O_2^+MF_6^-$$

No evidence was found for double protonation, i.e., $H_4O_2^{2+}$ formation, even when SbF_5 was used in a twofold excess. Instead, the polyanion $Sb_2F_{11}^-$ was formed according to

$$H_2O_2 + HF + 2SbF_5 \rightarrow H_3O_2^+Sb_2F_{11}^-$$

It is interesting to compare these results with those previously reported[24] for the N_2H_4–HF–TaF_5 system for which double protonation, i.e., $N_2H_6^{2+}(TaF_6^-)_2$ and $N_2H_6^{2+}TaF_7^{2-}$ formation, has been observed. Although other effects, such as the relative solubilities of the possible products, are certainly important, the predominant reason for the exclusive single protonation of H_2O_2 appears to be its decreased basicity. Whereas N_2H_4 is a weak base in aqueous solution (pK_b = 5.77), H_2O_2 is a weak acid (pK_a = 11.6). With increasing protonation, the basicity of the resulting cations further decreases, and $N_2H_5^+$ (pK_a = 6.1) becomes a weak and $N_2H_6^{2+}$ (pK_a = −1) a strong acid.[24,25] Whereas $N_2H_5^+$ has an acidity comparable to that of H_2S (pK_a = 7) which is known[5,6] to form stable H_3S^+ salts, $H_3O_2^+$ is too acidic to undergo further protonation to $H_4O_2^{2+}$.

Attempts to prepare $H_3O_2^+$ salts derived from BiF_5 were unsuccessful. The latter is a relatively strong oxidizer and is readily reduced by H_2O_2 in HF solution according to

$$BiF_5 + H_2O_2 \rightarrow BiF_3 + 2HF + O_2$$

When a twofold excess of BiF_5 was used, the following reaction was observed:

$$2BiF_5 + H_2O_2 \rightarrow BiF_3 \cdot BiF_5 + 2HF + O_2$$

The resulting $BiF_3 \cdot BiF_5$ product was shown by vibrational spectroscopy [Raman: 591 (10), 583 (4.6), 538 (1.5), 521 (0.1), 496 (0.6), 475 (sh), 232 (0.5, br), 120 (0.2, br) cm^{-1}. IR: 708 (w), 615 (s), 606 (sh), 575 (s), 550 (sh), 535 (vs), 400–500 (m, vbr) cm^{-1}] not to be a physical mixture of BiF_3[3,23] and BiF_5.[21,22] By analogy with the known BiF_3–SbF_5 and SbF_3–SbF_5 systems,[26-28] a $BiF_3 \cdot BiF_5$-type adduct appears most plausible. However, in view of the complexity of the products formed in the SbF_3–SbF_5 system,[27,28] a detailed characterization of this $BiF_3 \cdot BiF_5$ adduct was beyond the scope of this study.

Properties. The $H_3O_2^+SbF_6^-$, $H_3O_2^+Sb_2F_{11}^-$, and $H_3O_2^+AsF_6^-$ salts are white crystalline solids. X-ray powder patterns were taken for $H_3O_2^+Sb_2F_{11}^-$ but contained too many lines to allow indexing. All these $H_3O_2^+$ salts are of marginal thermal stability and were shown to undergo exothermic decomposition to the well-known[1] H_3O^+ salts according to

$$H_3O_2^+MF_6^- \rightarrow H_3O^+MF_6^- + {}^1/_2O_2$$

Of the above $H_3O_2^+$ salts, the AsF_6^- salt is the least stable and easily decomposes at room temperature. The $H_3O_2Sb_2F_{11}$ salt was found to be most stable. On the basis of DSC data, its decomposition starts with a small endotherm at 51 °C, followed by a large exotherm. In a sealed melting point capillary, decomposition accompanied by foaming was observed at about 65 °C. The thermal stability of $H_3O_2SbF_6$ is intermediate between those of $H_3O_2AsF_6$ and $H_3O_2Sb_2F_{11}$. It should be pointed out that the thermal stability of these $H_3O_2^+$ salts appears to decrease in the presence of free H_2O_2. Probably, the highly acidic $H_3O_2^+$ salt catalyzes the exothermic decomposition of H_2O_2, with the evolved heat promoting the decomposition of the $H_3O_2^+$ salt itself.

The reaction of $H_3O_2^+$ salts with fluorinating agents appeared interesting as a potential method for the generation of excited molecular oxygen (O_2*). Antimony pentafluoride or SbF_6^- were not strong enough oxidizers to fluorinate $H_3O_2^+$, and BiF_6^- reacted at too low a temperature with H_2O_2 to permit isolation of the desired $H_3O_2BiF_6$ salt. Therefore, the concept could not be directly tested to produce O_2* by the simple thermal decomposition of a salt composed of $H_3O_2^+$ and an oxidizing anion. However, when solid $H_3O_2Sb_2F_{11}$ was mixed at room temperature with a solid oxidizer, such as BiF_5 or Cs_2NiF_6, and when this mixture was heated to about 80 °C, a reaction occurred which was accompanied by green (5150-Å) chemiluminescence. This 5150-Å band did not exhibit detectable fine structure, and no additional bands were observed over the range 2000–10 000 Å. Consequently, the 5150-Å emission is not attributed to either vibrationally excited HF[29] or O_2.[30]

Nuclear Magnetic Resonance Spectra. The ^{19}F NMR spectrum of $H_3O_2SbF_6 \cdot 1.17SbF_5$ was recorded for a SO_2 solution at −90 °C. It showed resonances (ϕ 91, multiplet; 111, doublet of doublets; 133, quintet) characteristic[31] for $Sb_2F_{11}^-$. In addition, a weaker doublet at ϕ 102 was observed which is characteristic[31,32] for $SbF_5 \cdot SO_2$. The quintet part of this species could not be directly observed since it exhibits a chemical shift similar to that of the quintet of $Sb_2F_{11}^-$. The observation of some $SbF_5 \cdot SO_2$ is in excellent agreement with a previous report[31] that the highest polyanion observed for $SbF_6^- \cdot nSbF_5$ in SO_2 solution is $Sb_2F_{11}^-$, with any remaining SbF_5 being converted to $SbF_5 \cdot SO_2$. In addition to the signals due to $Sb_2F_{11}^-$ and $SbF_5 \cdot SO_2$ a weak unresolved signal was

Table I. Vibrational Spectra of $H_3O_2AsF_6$, $H_3O_2SbF_6$, and $H_3O_2Sb_2F_{11}$ and Their Assignments

obsd freq, cm^{-1} (rel intens)^a								
$H_3O_2AsF_6$		$H_3O_2SbF_6$			$H_3O_2Sb_2F_{11}$		assignt (pt group)	
IR (−196 °C)	Raman (−100 °C)	IR (−196 °C)	Raman (−110 °C)	Raman (25 °C)	IR (25 °C)	Raman (25 °C)	$HOOH_2^+$ (C_s)	SbF_6^- (O_h)^b
3440 sh	3440 (0.8)	3440 sh		3440 (0+)	3447 s	3435 (0+)	ν_1 (A′)	
3400–3150 vs		3400–3150 vs			3400 } vs, vbr		ν_7 (A″)	
3228 vs	3230 (0+) br	3230 vs			2600 }		ν_2 (A′)	
					2178 w			
1535 w	1547 (0.4)			1539 (0+)	1531 m	1530 (0+)	ν_3 (A′)	
1425 mw	1417 (1)	1421 mw		1426 (0+)	1420 ms	1419 (0+)	ν_4 (A′)	
		1280 w						
					1228 mw	1227 (0+)	ν_8 (A″)	
1115 m		1126 mw		1130 (0+) br	1137 s	1135 (0+)	ν_5 (A′)	
1100 } m, vbr		1065 sh						
900 }		965 sh						
		915 w						
870 m	873 (10)	876 mw	879 (8.6)	880 (5.4)		878 (1.5) }		
					869 m	868 (3) }	ν_6 (A′)	
						771 (0.2)		
728 vs	734 (39)		689 (5)		730 } vs, br	688 (10)		
	711 (1.5)		677 (10)	667 (10)		664 (0.5)		ν_1 (A_{1g})
665 vs	673 (9.5)	666 vs	642 (7)		640 }	649 (5.4)		
635 sh		615 s						
585 m		571 ms			594 mw			
	559 (2.4)		560 (2)					
550 ms		514 m		555 (0.7) br	565 m	576 (0.7)		ν_2 (E_g)
	528 (1.4)		530 (0.5)					
470 m		375 mw			508 m			
	400 (0+)		326 (1)			301 (2.5)		
388 vs		309 ms						
	370 (5.0)		283 (5)	282 (4)		280 (1)		ν_5 (F_{2g})
348 ms			263 (0.9)					
	316 (1.2)		226 (0.5)	226 (0+)		236 (2)		
	202 (2.5)		200 (1.5)					
	189 sh		174 (3.2)	167 (0+)		167 sh		
	149 sh		126 (2.4)	122 (0+)		144 (0.6)		
	129 (3.2)					112 sh		

[a] Uncorrected Raman intensities. [b] The assignments given for SbF_6^- are for the room-temperature Raman spectrum of $H_3O_2SbF_6$ in which SbF_6^- appears to be octahedral due to rotational averaging. In the low-temperature spectra the symmetry of the MF_6^- anion is much lower than O_h (see text).

observed at ϕ 106, in agreement with previous observations[31] on the *t*-BuF·3.8SbF$_5$ system. This signal is tentatively assigned to some $SbF_5{\cdot}H_2O$- or $SbF_5{\cdot}H_2O{\cdot}SbF_5$-type species.[33]

Attempts to observe the characteristic SbF_6^- signal in the ^{19}F NMR spectra of $H_3O_2SbF_6$ in different solvents were unsuccessful. In SO_2ClF the compound was insoluble. In either HF or HF acidified with AsF_5 only a single peak was observed due to rapid exchange between all fluorine-containing species. In SO_2 at −85 °C only two unresolved signals were observed at ϕ 107 and 127 with an area ratio of 4:1 indicating the possible presence of some $(SbF_5)_n{\cdot}H_2O$-type species.[33] The failure to observe SbF_6^- for $H_3O_2SbF_6$ in SO_2 parallels the previous report[31] by Bacon and co-workers who found that, unlike $CsSb_2F_{11}$, the $CsSbF_6$ salt is rather insoluble in SO_2 and $Sb_2F_{11}^-$ is the only observable anion in this solvent.

The ^1H NMR spectrum of $H_3O_2Sb_2F_{11}$ in CH_3SOCH_3 solution showed a single broad asymmetric peak. Its line width and chemical shift were temperature dependent. At 20 °C its line width at half-height was 81 Hz, and δ was 11.80 relative to external Me_4Si with a shoulder on the upfield side. At 0 °C the line narrowed to 36 Hz and broadened again at −60 °C to 72 Hz. With decreasing temperature the line became more symmetric and shifted downfield (δ 12.20 at −60 °C). The failure to observe two different types of protons and the variation of the observed line widths indicate rapid proton exchange for $H_3O_2^+$. The assignment of the observed signal to $H_3O_2^+$ is supported by its large downfield shift. For comparison, 99% pure H_2O_2 exhibits between 20 and −30 °C a chemical shift of δ 10.3 relative to external Me_4Si. On protonation, this signal is expected to be shifted further downfield, as has previously been demonstrated[34] for numerous other species. The signal assigned to $H_3O_2^+$ also occurs significantly downfield from those previously reported for H_3O^+ [1,34,35] and $SbF_5{\cdot}H_2O$[33] and therefore cannot be due mainly to these species.

In HF–AsF_5 solution at −80 °C, only a single broad signal at δ 11.06 was observed for $H_3O_2Sb_2F_{11}$ indicating rapid proton exchange between $H_3O_2^+$ and the HF solvent. In SO_2 solutions of $H_3O_2Sb_2F_{11}$, two lines at δ 9.94 and 11.84, respectively, were observed at −80 °C. The relative intensity of the δ 9.94 signal varied from sample to sample and also as a function of temperature. With decreasing temperature the peak area of the δ 9.94 signal decreased more rapidly than that of the δ 11.84 signal. These observations suggest that the two signals cannot belong to the same species. By comparison with previous reports,[1,34,35] the δ 9.94 signal is assigned to H_3O^+, and the more intense δ 11.84 signal is attributed to $H_3O_2^+$, in good agreement with our observations for the CH_3SOCH_3 solution. The line width of the δ 11.84 signal was temperature dependent and showed a minimum (~7 Hz) at about −60 °C, but no splittings could be observed. With increasing temperature, the δ 9.94 and 11.84 signals moved closer together, indicating the onset of chemical exchange between the two species.

The observations of H_3O^+ in the proton spectrum and possibly of a small amount of an $(SbF_5)_n{\cdot}H_2O$ adduct in the fluorine spectrum suggest that $H_3O_2Sb_2F_{11}$ may undergo either a redox reaction or decomposition in SO_2 solution.

Vibrational Spectra. The infrared and Raman spectra of $H_3O_2AsF_6$, $H_3O_2SbF_6$, and $H_3O_2Sb_2F_{11}$ are shown in Figures

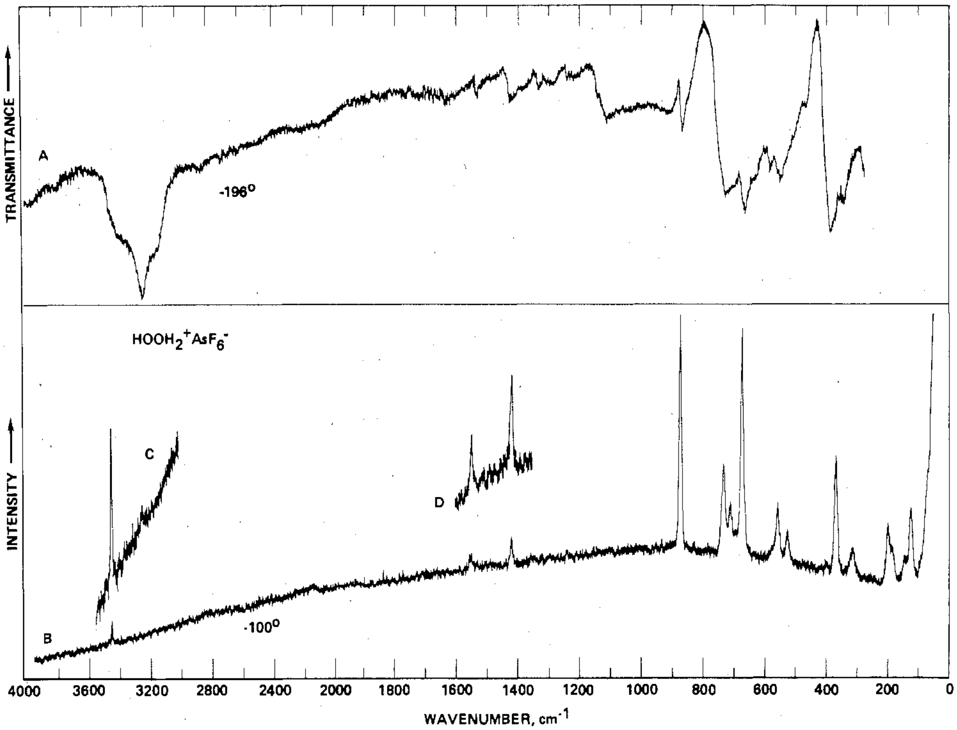


Figure 1. Vibrational spectra of $H_3O_2^+AsF_6$: trace A, infrared spectrum of the solid as a dry powder between CsI disks recorded at −196 °C; trace B, Raman spectrum of the solid in a glass tube recorded at −100 °C with a spectral slit width of 8 cm^{-1} and a sensitivity of 100 000; inserts C and D were recorded with a spectral slit width of 10 cm^{-1} at sensitivities of 380 000 and 250 000, respectively.

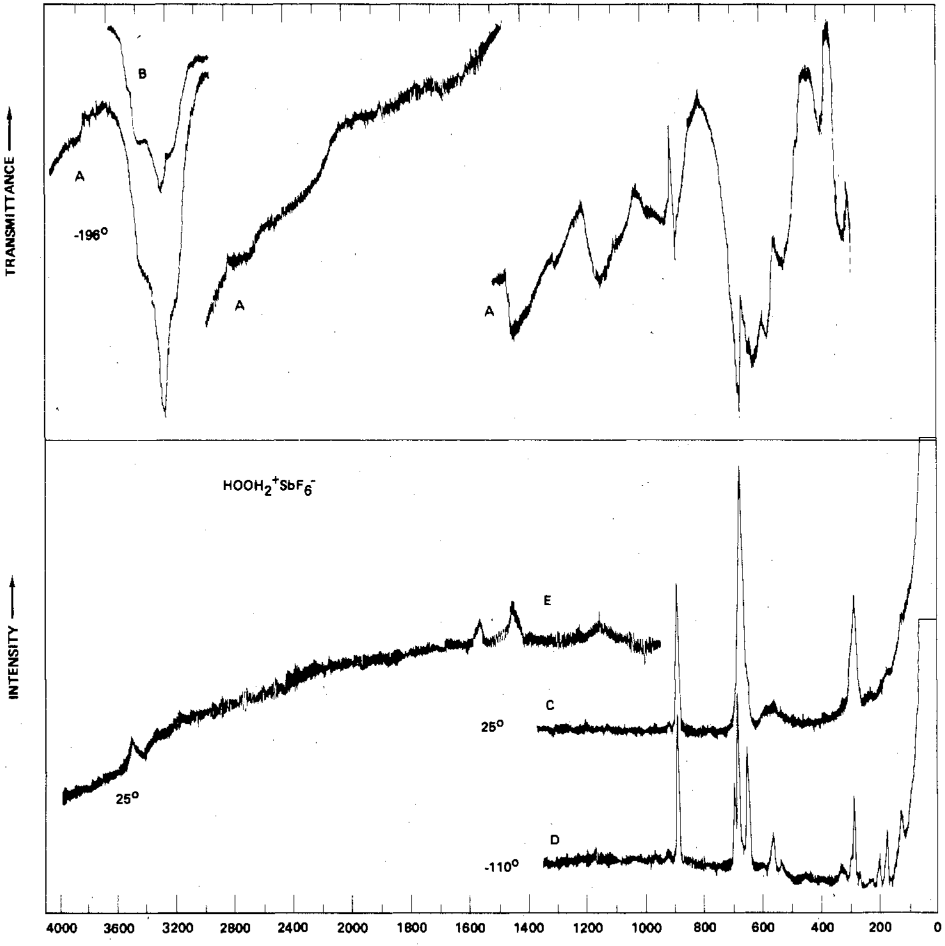


Figure 2. Vibrational spectra of $H_3O_2^+SbF_6^-$: traces A and B, infrared spectra of the solid recorded at −196 °C at two different sample concentrations; traces C and E, Raman spectra of the solid recorded at 25 °C with spectral slit widths of 5 and 10 cm^{-1}, respectively; trace D, Raman spectrum of the solid recorded at −110 °C.

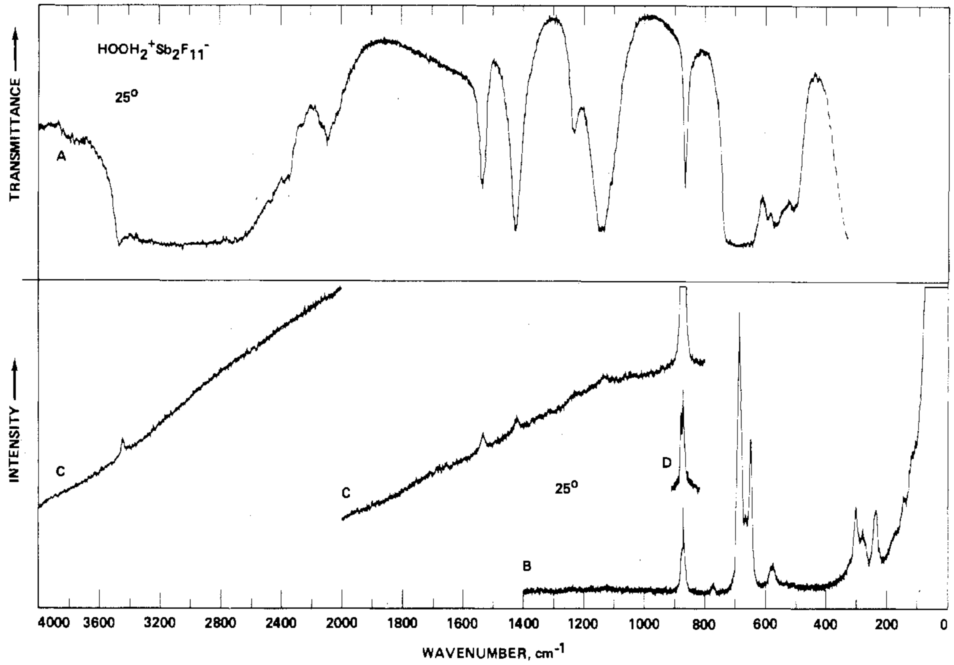


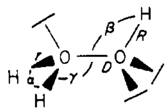
Figure 3. Vibrational spectra of $H_3O_2^+Sb_2F_{11}^-$: trace A, infrared spectrum of the solid as a dry powder between pressed AgCl disks; traces B, C, and D, Raman spectra of the solid recorded at 25 °C with spectral slit widths of 5, 10, and 2.5 cm^{-1}, respectively.

1, 2, and 3, respectively, and the observed frequencies are summarized in Table I. For the thermally more stable antimonate salts, spectra could be obtained at ambient temperature without the samples undergoing significant decomposition to the corresponding H_3O^+ salts. For $H_3O_2AsF_6$, only low-temperature spectra could be obtained.

The vibrational spectra of $H_3O_2SbF_6$ (see Figure 2) showed a pronounced temperature dependence. At room temperature, the Raman spectrum (traces C and E) exhibited three bands at 667, 555, and 282 cm^{-1}, respectively, characteristic for octahedral SbF_6^-.[1,5,7,18,19] When the sample temperature was lowered, the number of bands due to SbF_6^- significantly increased, indicating that the symmetry of SbF_6^- became lower than O_h. This transition was found to be reversible and to occur close to room temperature. Similar transitions have previously been observed for the corresponding H_3O^+,[1] D_3O^+,[36] and O_2^+[37] salts. They can be attributed to rapid motions of the ions in the crystal lattice at room temperature, causing rotational averaging. With decreasing temperature, these motions are frozen out, causing the observed effects of symmetry lowering of the anions. Since the symmetry of the corresponding cations is low (no degeneracies), their vibrational spectra are much less affected.

Assignments for the $H_3O_2^+$ Cation. The assignments for $H_3O_2^+$ were made on the basis of the following arguments. With the exception of the O–O torsional mode, which by comparison with the known frequency[38] of the corresponding N–O torsion in the isoelectronic H_2NOH molecule is expected to occur below 400 cm^{-1}, all of the fundamental vibrations of $H_3O_2^+$ should have frequencies higher than those of the anions. The bands due to the anions can be further identified by comparison with the ambient and low-temperature spectra previously reported for the corresponding H_3O^+[1] and $NH_2F_2^+$[7] salts. In view of the complexity of the low-temperature anion spectra, in Table I only the room-temperature Raman spectrum of rotationally averaged SbF_6^- has been assigned. Keeping in mind that $Sb_2F_{11}^-$ spectra strongly depend on the nature of the countercation, the room-temperature spectrum of $Sb_2F_{11}^-$ in $H_3O_2Sb_2F_{11}$ is in fair agreement with those previously observed for this anion in numerous other salts.[39-43]

Thus, the intense bands occurring above 800 cm^{-1} should belong to $H_3O_2^+$. By comparison with the known trans structure of isoelectronic H_2NOH,[44] this cation should have the following structure of symmetry C_s



Consequently, nine fundamentals (6 A′ + 3 A″) are expected for $H_3O_2^+$. These fundamentals should all be active in both the infrared and the Raman spectra. Of these, eight should occur above 800 cm^{-1} (see above). As can be seen from Figures 1–3 and Table I, indeed eight bands were observed in this frequency region. An approximate description of the $H_3O_2^+$ fundamental vibrations is given in Table II. There should be four stretching modes. Three of these should involve hydrogen ligands, while the fourth one is the oxygen–oxygen stretching mode.

The three hydrogen–oxygen stretching modes should occur above 2500 cm^{-1}. Their assignment, however, is somewhat complicated. By comparison with the known spectra of related molecules, such as CH_3NH_2,[45] H_2NOH,[38,46] H_2O, CH_3OH, and $>CH_2$ group containing molecules,[47] we would expect the H_2O– group to exhibit two intense infrared bands in the OH stretching region. Of these two, the antisymmetric stretching

Table II. Comparison of the Vibrational Spectrum of $H_3O_2^+$ with Those of Isoelectronic H_2NOH and $H_3N_2^-$

assignt for H_2XYH in pt group C_s		approx descript of mode	obsd freq, cm^{-1}		
			H_2-OOH^+	H_2-NOH[b]	H_2-NNH^- [c]
A′	ν_1	$\nu(YH)$	3440	3656	3202
	ν_2	$\nu_{sym}(XH_2)$	3229	3297	3100
	ν_3	$\delta_{sciss}(XH_2)$	1536	1605	1599
	ν_4	$\delta(XYH)$ in plane	1421	1357	1330
	ν_5	$\delta_{wag}(XH_2)$	1136	1115	1103
	ν_6	$\nu(XY)$	875	895	847
A″	ν_7	$\nu_{asym}(XH_2)$	3275	3350	3155
	ν_8	$\tau(XH_2)$	1228	1297	1232
	ν_9	$\tau(XY)$	[386][a]	386	[386][a]

[a] Estimated frequency values. [b] Data from ref 46, but revised according to ref 38. [c] Data from ref 48, but with revised assignments for ν_4 and ν_5.

mode should have a frequency 50–100 cm^{-1} higher than that of the symmetric stretching mode. In the Raman spectrum the symmetric stretching mode should be much more intense than the antisymmetric one. The unique –OH stretching mode should be of considerably lower infrared intensity than the two $-OH_2$ stretching modes.

Inspection of the Raman spectrum of $H_3O_2AsF_6$ shows a very narrow Raman line at 3440 cm^{-1} and a barely detectable broad line at 3230 cm^{-1}. Since the 3440-cm^{-1} Raman line shows only a rather weak infrared counterpart while the 3230-cm^{-1} one exhibits a very intense infrared counterpart and since no intense infrared band occurs above 3440 cm^{-1}, the 3440-cm^{-1} band is assigned to the unique –OH stretch and the 3230-cm^{-1} band to the symmetric $-OH_2$ stretch of H_2OOH^+. The 3228-cm^{-1} infrared band exhibits a shoulder on both its high- and its low-frequency side. Instead of assigning these two shoulders to two separate bands, one might equally well attribute them to a single broad band onto which the sharper 3228-cm^{-1} band is superimposed. Such a broad band might be expected for the antisymmetric $-OH_2$ stretching mode, and its center (3275 cm^{-1}) results in a frequency value which agrees well with the above predicted frequency difference between the symmetric and the antisymmetric $-OH_2$ stretching mode. In the spectrum of $H_3O_2SbF_6$ the situation is almost identical. For $H_3O_2Sb_2F_{11}$, the infrared counterpart to the 3435-cm^{-1} Raman band is also rather narrow and occurs at the very edge of the intense and extremely broad infrared band. These observations seem to support our assignments, although it is not obvious why the Raman line for the unique –OH stretch should be so much sharper than that for the symmetric $-OH_2$ stretch. If the –OH stretch and the symmetric $-OH_2$ stretch would have comparable Raman line widths, the latter should have a greater peak height than the –OH stretch and should be easily observed.

Whereas the modes involving mainly O–H bonds should be of low Raman and of high infrared intensity, the O–O stretching mode should be quite intense in the Raman spectrum and occur in the frequency range 800–1000 cm^{-1}. It is therefore assigned to the strong Raman line occurring in all samples between 868 and 880 cm^{-1}. As expected, this band shows a counterpart of medium intensity in the infrared spectra. In the spectra of $H_3O_2SbF_6 \cdot 1.17SbF_5$ ("$H_3O_2Sb_2F_{11}$") this band shows a splitting into two components, separated by about 10 cm^{-1}. This splitting might be due to the sample not having an exact 1:2 stoichiometry and therefore containing a mixture of different polyantimonates. For the two well-defined 1:1 adducts $H_3O_2AsF_6$ and $H_3O_2SbF_6$, no splittings of this band could be detected.

Of the five deformation modes expected for $H_3O_2^+$ of symmetry C_s, four involve the O–H bonds and should occur in the frequency range 1000–1700 cm^{-1}. Indeed, four infrared bands were observed in this frequency range for $H_3O_2Sb_2F_{11}$ with counterparts in the Raman spectrum. Their assignment to the individual modes (see Table II) was made by analogy to those known[47] for related molecules, such as H_2O, CH_3OH, CH_3NH_2, and CH_2X_2.

The $-OH_2$ scissoring mode should have the highest frequency and occur between 1500 and 1600 cm^{-1}. It is therefore assigned to the band observed in most spectra at about 1535 cm^{-1}. The $-XH_2$ in-plane deformation mode is usually very intense in the infrared spectrum and occurs for H_2NOCH_3[38] and H_2NOH[38,46] at 1150 and 1115 cm^{-1}, respectively. For H_2OOH^+ it is therefore assigned to the strong infrared band at about 1130 cm^{-1}. The $-XH_2$ twisting mode is usually very weak and occurs in H_2NNH_2, H_2NOH,[38] and H_2NNH^-[48] at 1260, 1297, and 1232 cm^{-1}, respectively. It is therefore assigned to the medium weak band observed for $H_3O_2Sb_2F_{11}$ at 1228 cm^{-1}. There is only one frequency (~1420 cm^{-1}) left for assignment to the –OOH in-plane deformation mode. This assignment is in fair agreement with the value of 1345 cm^{-1} attributed to the corresponding –COH deformation in CH_3OH.[47]

Table III. Geometries[a] Used for the Normal-Coordinate Analyses of the Isoelectronic H_2XYH Molecules and Ions

	H_2OOH^+	H_2NOH	H_2NNH^-
r (XH)	0.98	1.016	1.03
R (YH)	0.99	0.962	1.03
D (XY)	1.475	1.453	1.47
α (∡HXH)	107.06	107.06	107.06
β (∡XYH)	101.22	101.22	101.22
γ (∡HXY)	103.15	103.15	103.15

[a] Bond distances in Å and angles in degrees.

The fifth deformation mode, the O–O torsion, is expected to occur in the 300–400-cm^{-1} frequency region. Since numerous bands due to either the anion or anion–cation interactions occur in this region, no assignments are proposed at this time for this mode.

In summary, with the exception of the O–O torsional mode, all fundamentals of H_2OOH^+ have been observed and assigned. The assignments are summarized in Table III and are compared to those of isoelectronic H_2NOH[38,46] and H_2NNH^-.[48] The similarity of the vibrational spectra of H_2OOH^+, H_2NOH, and H_2NNH^- suggests that the two ions are isostructural with NH_2OH for which a trans structure of symmetry C_s was established[44] by microwave spectroscopy and confirmed[49] by ab initio molecular orbital theory. As expected for salts containing cations with hydrogen ligands and anions with fluorine ligands, strong cation–anion interactions were observed. These result in a lowering of the oxygen–hydrogen stretching frequencies and cause splittings of the anion bands in the spectra at low temperature at which rotational-averaging processes are frozen out.

Normal-Coordinate Analyses. Normal-coordinate analyses were carried out for H_2OOH^+ and the isoelectronic H_2NOH molecule and H_2NNH^- anion to support the above assignments and the contention that the three isoelectronic species are isostructural. Furthermore, it was important to establish whether the fundamental vibration assigned to the stretching mode of the two central atoms is highly characteristic and therefore can be taken as a direct measure for their bond strength.

For the computation of the force fields, the vibrational frequencies and assignments of Table II were used. The required potential and kinetic energy metrics were computed by a machine method[50] using the geometries given in Table III. Since the frequency of the $X-Y$ torsion mode ν_9 (A″) is unknown for both H_2OOH^+ and H_2NNH^- and since, on the basis of its expected low frequency, coupling with other modes should be negligible, this fundamental was omitted from the normal-coordinate analyses. For H_2OOH^+ and H_2NNH^-, the bond angles were assumed to be identical with those known[44] for H_2NOH, and the bond lengths were estimated by comparison with those known for the similar H_2O_2 and N_2H_4 molecules. The bending coordinates were weighted by unit (1 Å) distance.

The force constants of these H_2XYH-type species were adjusted by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies. Since in the A′ block the X–Y stretching force constant F_{66} was found to strongly depend on the values of the stretch–bend interaction constants F_{46} and F_{56}, the diagonal-symmetry force constants were computed as a function of F_{46} and F_{56}. As can be seen from Figures 4 and 5, the values of YH (F_{11}) and XH_2 (F_{22}) stretching force constants are unaffected by the choice of F_{46} and F_{56}, but the X–Y stretch (F_{66}) depends strongly on the choice of F_{46} and F_{56}. In the absence of additional ex-

Table IV. Anharmonic Symmetry Force Constants[a] and Potential Energy Distribution[b] of H_2OOH^+, H_2NOH, and H_2NNH^- [c]

		symmetry force constants				PED		
		H_2OOH^+	H_2NOH	H_2NNH^-		H_2OOH^+	H_2NOH	H_2NNH^-
A′	$F_{11} = f_R$	6.607	7.46	5.675	F_{11}	100	100	100
	$F_{22} = f_r + f_{rr}$	5.92	6.13	5.42	F_{22}	100	100	100
	$F_{33} = f_\alpha$	0.628	0.733	0.748	F_{33}	95	99	99
	$F_{44} = f_\beta$	1.054	0.902	0.977	F_{44}	94	98	98
	$F_{55} = f_\gamma + f_{\gamma\gamma}$	0.715	0.72	0.728	F_{55}	95	97	96
	$F_{66} = f_D$	3.93	3.87	3.15	F_{66}	101	99	103
	$F_{35} = 2^{1/2} f_{\alpha\gamma}$	0.1	0.1	0.1				
	$F_{46} = f_{D\beta}$	0.2	0.2	0.2				
	$F_{56} = 2^{1/2} f_{D\gamma}$	0.3	0.3	0.3				
A″	$F_{77} = f_r - f_{rr}$	5.884	6.089	5.401	F_{77}	100	100	100
	$F_{88} = f_\gamma - f_{\gamma\gamma}$	0.782	0.922	0.850	F_{88}	100	100	100

[a] Stretching constants in mdyn/Å, deformation constants in mdyn Å/rad^2, and stretch-bend interaction constants in mdyn/rad. [b] Percent contributions. Contributions of less than 9% to the PED are not listed. [c] Computed with the frequencies and assignments of Table III; all interaction constants except for F_{35}, F_{46}, and F_{56} were assumed to be zero.

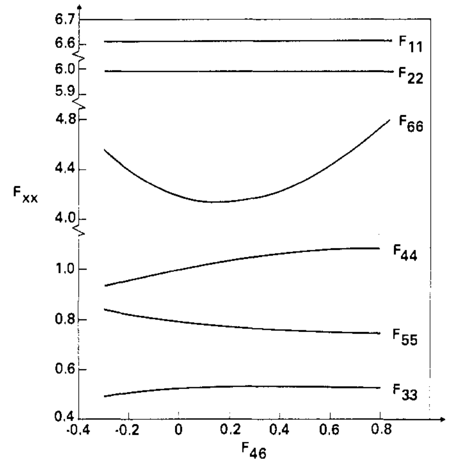


Figure 4. Diagonal symmetry force constants (stretching constants F_{11}, F_{22}, and F_{66} in mdyn/Å and deformation constants F_{33}, F_{44}, and F_{55} in mdyn Å/rad^2) of the A′ block of H_2OOH^+ as a function of the stretch–bend interaction constant F_{46} (in mdyn/rad). All the remaining off-diagonal symmetry force constants were assumed to be zero.

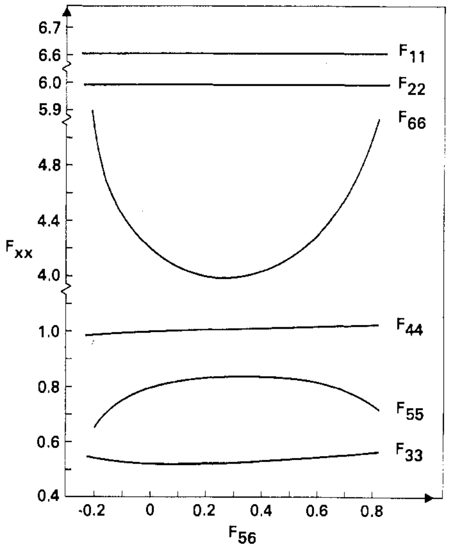


Figure 5. Diagonal symmetry force constants of the A′ block of H_2OOH^+ as a function of F_{56}.

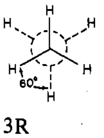
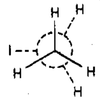
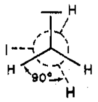
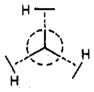
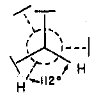
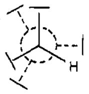
perimental data, such as oxygen isotopic shifts, the uncertainty in the value of F_{66} obtained by underdetermined force fields must therefore be considered to be substantial. In the absence of such additional data, we have chosen for the isoelectronic H_2XYH series a force field which resulted in a highly characteristic potential energy distribution (PED) for all fundamentals (see Table IV). The X–Y stretching force constants obtained in such a manner represent minimal values but could be higher by as much as 0.4 mdyn/Å if larger positive values are assumed for F_{46} and F_{56}. A moderate size value was found necessary for F_{35} to obtain a characteristic PED for ν_3 and ν_5.

In a recent paper, Botschwina and co-workers have reported[51] a partial ab initio harmonic force field for H_2NOH. Since this type of computation can yield valuable information about the off-diagonal force constants, a comparison with the results of Table IV appeared interesting. Botschwina et al. report a value of 0.629 mdyn/rad for F_{46} (using the force constant designation of Table IV of our work) and predict values of 8.1 ± 0.1 mdyn/Å and 0.9 ± 0.05 mdyn Å/rad^2 for F_{11} and F_{33}, respectively. The latter two values and the positive sign of F_{46} are in fair agreement with the anharmonic force field of Table IV, although the value computed[51] for F_{46} appears to be high. A calculation of a force field with $F_{46} = 0.63$ and $F_{56} = 0$ resulted in ν_5 and ν_6 becoming almost equal mixtures of F_{55} and F_{66} and an unacceptably high value of about 5 mdyn/Å for F_{66}. Assuming a positive value for F_{56} resulted in even less acceptable force constants.

A comparison of the results of Table IV shows that the force fields of isoelectronic H_2OOH^+, H_2NOH, and H_2NNH^- are indeed very similar and suggests that all members of this series are isostructural. The small deviations observed within the series (higher values of F_{11}, F_{22}, and F_{77} for H_2NOH) can be readily explained. For H_2NOH, gas-phase frequencies of the isolated molecule were used, whereas in the H_2OOH^+ and H_2NNH^- salts the anion–cation interactions lower the stretching frequencies somewhat (see above).

The question whether ν_6, the fundamental vibration assigned to the stretching mode of the two central atoms, is highly characteristic or not also needed to be answered. The fact that ν_6 is of very high Raman intensity, whereas ν_5 is barely observable, and the known high polarizabilities of the central atoms relative to those of the hydrogen ligands argue strongly in favor of ν_6 being predominately the O–O stretching mode. Furthermore, the value of the O–O stretching force constant F_{66} (3.93 mdyn/Å) and the highly characteristic nature of ν_6 (101% F_{66}) of H_2OOH^+ are in excellent agreement with the previously reported[52] findings for gaseous HOOH ($F_{O\text{-}O}$ = 3.776 mdyn/Å; $\nu_{O\text{-}O}$ = 105% of $F_{O\text{-}O}$). For solid HOOH, a value ($F_{O\text{-}O}$ = 3.999 mdyn/Å) was found[53] which is slightly higher than that in H_2OOH^+. A further argument in favor of highly characteristic X–Y stretching frequencies in these and closely related molecules is based on the vibrational spectra observed for deuterated molecules, such as DOOD.[52,53] If the fundamental assigned to the O–O stretch in HOOH would contain strong contributions from X–H bending modes, its frequency should significantly decrease on deuteration.

Table V. Preferred Rotational Isomers, Number of Vicinal Ligand Repulsions (R), and Attractions (A), and Frequencies (cm^{-1}) of the Stretching Mode of the Two Central Atoms of $H_3NNH_3^{2+}$,[a] $H_3NNH_2^+$,[b] H_2NNH_2,[c] H_2NNH^-,[d] H_2OOH^+,[d] HOOH,[e] and HOO^- [f]

					
3R	2R-1A	1R-2A	3A	2A-1R	1A-2R
$H_3NNH_3^{2+}$	$H_3NNH_2^+$	H_2NNH_2	H_2NNH^-		
1048[g]	949[h]-968[i]	850-938[j]	847[k]		
			H_2OOH^+	HOOH	HOO^-
			875[l]	864-881[m]	836[n]

[a] Geometry of preferred rotational isomer is based on that of isoelectronic C_2H_6.[55] [b] Geometry assumed to be analogous to that of isoelectronic CH_3NH_2.[56] [c] Reference 57. [d] Geometry is based on that of isoelectronic H_2NOH.[44] [e] Reference 58. [f] For HOO^-, a preferred rotational isomer does not exist. The structure is given exclusively for didactic purposes. [g] From Raman spectrum of $N_2H_6F_2$ in anhydrous HF solution (B. Friec and H. H. Hyman, *Inorg. Chem.*, 6, 2233 (1967)). [h] From infrared spectrum of solid $(N_2H_5)TaF_7$.[24] [i] From Raman spectrum of N_2H_5Cl in aqueous HCl solution (J. T. Edsall, *J. Chem. Phys.*, 5, 225 (1937)); see also J. C. Decius and D. P. Pearson, *J. Am. Chem. Soc.*, 75, 2436 (1953). [j] The assignments for the N-N stretching mode in N_2H_4 are not well established and significantly differ for the gas and condensed phases (see example ref 48 and J. R. Durig, S. F. Bush, and E. E. Mercer, *J. Chem. Phys.*, 44, 4238 (1966)). The latter authors assigned the N-N stretch in N_2H_4 to bands in the 1087–1126-cm^{-1} frequency region which does not fit the general trends listed in this table. [k] From infrared spectrum of solid NaN_2H_3.[48] [l] This work. [m] Reference 12. [n] Reference 10.

In summary, it appears justified to assume that the fundamentals, assigned to the stretching modes of the two central atoms in these molecules and ions, are highly characteristic and that a highly characteristic PED might be a good criterion for selecting a plausible force field.

Influence of Progressive Protonation on the Bond Strength of the Two Central Atoms. It seemed interesting to examine how in an H_mXYH_n-type species the replacement of a free valence electron pair of a central atom by a hydrogen ligand influences the strength of the X–Y bond. Further interest was added to this problem by the fact that these X–Y bonds are single bonds, thus resulting in hindered rotation and rotational conformers. In the literature,[8,54] the concept has been advanced that in a singly bonded X–Y system the replacement of a free valence electron pair on X or Y by a bonded ligand will diminish the overall ligand or electron-pair repulsions, thereby strengthening the X–Y bond. The results of the present study combined with previous literature data offered an excellent opportunity to examine the validity of this simple repulsion concept for the progressively protonated series HOO^-, HOOH, and H_2OOH^+, which is isoelectronic with H_2NNH^-, followed by H_2NNH_2, $H_2NNH_3^+$, and $H_3NNH_3^{2+}$.

For this series the energetically most favored rotational isomers and the stretching frequencies of the two central atoms are summarized in Table V. Stretching frequencies are preferred over force constants because for HOOH,[53] H_2OOH^+, and H_2NNH^- these frequencies are highly characteristic and because of the lack of reliable fully determined force fields for most of these species. In Table V, frequency ranges are given for HOOH, $H_3NNH_2^+$, and N_2H_4. For the first two, these ranges are caused by the fact that the frequencies vary somewhat for different phases. For N_2H_4, the large given range is mainly due to the uncertainty in the assignment of the N–N stretching mode (see footnote *k* of Table V). In spite of these limitations, inspection of the listed frequencies reveals not only that there is a definite X–Y stretching frequency increase with progressive protonation but also that the increase of the O–O stretching frequency from HOO^- to H_2OOH^+ (30 cm^{-1}) is much smaller than that (201 cm^{-1}) encountered for the H_2NNH^- to $H_3NNH_3^{2+}$ part of the series.

This marked difference is difficult to explain by the simple free valence electron pair repulsion concept[8,54] which should result in a more uniform trend and cannot account for the eclipsed structure of H_2NOH. A better explanation for the observed trends can be given on the basis of the following considerations. (i) The preferred rotational isomers (see Table V) indicate that in an H_mXYH_n-type species, in which the X and Y central atoms possess free valence electron pairs, attractive forces exist between a free valence electron pair on one central atom and a hydrogen ligand bonded to the other central atom. In terms of molecular orbital theory, this effect can be considered to be the result of both dipolar attraction and back-donation from lone-pair orbitals of one central atom into antibonding orbitals of the other.[49] On the other hand, free valence electron pairs on X are repelled by free pairs on Y, and the same holds for vicinal hydrogen ligands. These effects explain the eclipsed configuration of H_2NOH,[44] the staggered one of C_2H_6,[55] and the gauche ones[56-58] of the remaining species. (ii) When going from HOO^- to $H_3NNH_3^{2+}$, one observes that the number of repulsions between vicinal ligands (including the free valence electron pairs) decreases from two for HOO^- to zero for H_2OOH^+ and H_2NNH^- and then increases again to three for $H_3NNH_3^{2+}$. (iii) It is known that for peroxides a weakening of the oxygen–ligand bonds results in a strengthening of the O–O bond (FOOF, ν_{O-O} 1257 cm^{-1}; HOOH, ν_{O-O} 864 cm^{-1})[59,12] and vice versa. Furthermore, it is known[8] that the $^{\delta-}X-H^{\delta+}$ polarity of an X–H bond increases by the addition of a second H^+ to X. This increase in bond polarity upon progressive protonation weakens the X–H bonds and therefore should strengthen the X–X bond. In addition, protonation is expected to shift more s character to the orbital involved in the X–X bond, thereby strengthening this bond. In our opinion, these two effects are the major reasons for the observed increase of the X–X stretching frequency within this series.

The fact that the stepwise increases within the series of Table V are small to the right of H_2XXH and large to the left of it suggests that the attractions between a free valence electron pair and a vicinal hydrogen ligand are at a maximum for H_2XXH and counteract the general polarity effect caused by the progressive protonation. This explanation seems plausible because both dipole interaction and back-donation should decrease the $^{\delta-}X-H^{\delta+}$ polarity of the X–H bond by transferring electron density from the free valence electron pair orbital to the vicinal hydrogen ligand. Although this picture is oversimplified and neglects other effects, such as possible changes in hybridization, it can nevertheless qualitatively account for the observed trends within this series. Molecular orbital calculations would be desirable but were beyond the scope of this study. In view of the great difficulties encountered with FOOF,[60] such calculations might not be trivial.

The above analysis indicates that the replacement of a free valence electron pair on one of the two central atoms by a hydrogen ligand could either decrease *or* increase the vicinal ligand (or electron pair) repulsion. The direction of the effect depends on whether the two central atoms possess less than three or three and more hydrogen ligands. With less than three hydrogen ligands, a free pair–free pair repulsion is replaced by a free pair–XH bond attraction, whereas with three or more hydrogen ligands an attraction is replaced by a vicinal hydrogen–hydrogen ligand repulsion. The importance of the attractive forces in this type of molecule is in agreement with the results from molecular orbital calculations.[49,61]

The above results suggest that the previously proposed[8,54] simple free valence electron pair repulsion concept applies only to H_mXYH_n species with $\sum(m + n) < 3$. In these limited cases, replacement of a free valence electron pair by a ligand will result in decreased ligand–ligand repulsion. However, this decreased repulsion counteracts the polarity effect and therefore does not strengthen but actually weakens the bond between the two central atoms. Consequently, the simple free valence electron pair repulsion concept cannot account, even in these limited cases, for the observed increase in the stretching frequency of the two central atoms.

The above results show that for a comparison, such as that given in Table V, a large enough number of molecules and ions must be available to have confidence in the observed trends. Furthermore, the assignments must be well established, the fundamental vibrations used must be highly characteristic, and interionic or intermolecular effects, such as hydrogen bridging in ionic solids or condensed phases, must be less pronounced than the trends to be observed. Finally, force constants should be compared only if their differences are significantly larger than their uncertainties.

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Registry No. $H_3O_2^+Sb_2F_{11}^-$, 70850-27-0; $H_3O_2^+SbF_6^-$, 70850-28-1; $H_3O_2^+AsF_6^-$, 70850-29-2; H_2NNH^-, 25415-88-7; H_2NOH, 7803-49-8; AsF_5, 7784-36-3; SbF_5, 7783-70-2; BiF_5, 7787-62-4; H_2O_2, 7722-84-1; HF, 7664-39-3; $BiF_3 \cdot BiF_5$, 70850-25-8.

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