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Synthesis of Hydrogen Polyoxides H_2O_4 and H_2O_3 and Their Characterization by Raman Spectroscopy

Alexander V. Levanov,*[a] Dmitri V. Sakharov,[b] Anna V. Dashkova,[a] Ewald E. Antipenko,[a] and Valeri V. Lunin[a]

Dedicated to the memory of Professor N. I. Kobozev (1903–1974)

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Hydrogen tetroxide (H_2O_4) and hydrogen trioxide (H_2O_3) have been prepared in relatively large quantities as components of peroxy radical condensates. The polyoxides were characterized by the Raman spectra of the oxygen framework. Lines at 500, 756, and 878 cm^{-1} correspond to skeletal oscillations of H_2O_3 in the condensate (OOO bend, asymmetric OO stretch, symmetric OO stretch). Lines at 449, 589, 624, 827, and 865 cm^{-1} match the skeletal vibrations of H_2O_4 (OOO bend 1, OOO bend 2, center OO stretch, asymmetric OO stretch, symmetric OO stretch). The line of the O_4 torsion vibration of hydrogen tetroxide was not observed experimentally. The assignment was confirmed by B3LYP/6-31+G(d,p) calculations of the vibrational spectra. According to the information available in the literature, this work is the only report of the preparation of H_2O_4 in significant concentrations and its Raman spectrum. For the first time convincing evidence is provided for the existence of hydrogen tetroxide (in low-temperature solids).

Introduction

Hydrogen is the most widespread element in the universe, and oxygen is the same on Earth. However, there are only a few compounds of these two elements: H_2O, H_2O_2, unstable radicals OH, HO_2, and HO_3, and hydrogen polyoxides H_2O_3 and H_2O_4. The polyoxides are of interest from the viewpoint of chemical structure theory as molecules with catenated oxygen chains and higher members of the homological series starting from H_2O and H_2O_2. Furthermore, H_2O_3 and H_2O_4[1] are intermediates of the important radical/radical reactions $HO_2^{\cdot} + OH^{\cdot} \rightarrow H_2O + O_2$ and $HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2$. These reactions appear almost everywhere on Earth and are of great importance in atmospheric chemistry, combustion and flame chemistry, oxidation reactions in living organisms, aqueous radiochemical processes, and aqueous ozone chain reactions. It was found that H_2O_3 is formed during the thermal reaction between hydrogen peroxide and ozone[2] as well as in the reaction of ozone with a number of organic compounds.[3] There is evidence that H_2O_3 may play an important role in immune reactions in living organisms.[4]

Questions such as "how many members are there in the homological series H_2O, H_2O_2, ..., H_2O_n?"[5] and "what are the properties of polyoxides H_2O_n ($n > 2$) if they exist?"[6] have occupied the minds of chemists since the end of the 19th century. H_2O_3 was first mentioned in 1880 by Berthelot as a possible intermediate in the decomposition of hydrogen peroxide.[7] H_2O_4 was proposed in 1895 by Mendeleev as a higher member of the H_2O_n homological series by analogy with the corresponding sulfur compounds H_2S, H_2S_2, H_2S_3, and H_2S_4.[8] A detailed review of the subject prior to 1968 has been written by Venugopalan and Jones.[9]

The experimental investigation of H_2O_3 and H_2O_4 is closely connected with research on the so-called peroxy radical condensate. This condensate is a glassy solid, obtained on a cold surface (80 K) by condensation of water, hydrogen peroxide vapor or H_2/O_2 mixtures dissociated in a low-pressure electrical discharge and by low-temperature interaction of hydrogen atoms with oxygen or with ozone. Upon heating above 150 K, the condensate decomposes vigorously to yield large amounts of gaseous oxygen and concentrated hydrogen peroxide solution. The formation of hydrogen peroxide from a low-temperature reaction of hydrogen atoms with molecular oxygen was detected by Boehm and

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[a] Department of Chemistry, M. V. Lomonosov Moscow State Unversity
Leninskiye Gory 1, Building 3, 119991 Moscow, Russia
Fax: +7-495-939-4575
E-mail: levanov@kge.msu.ru
[b] A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences
Leninsky Prospect 29, 119991 Moscow, Russia

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Bonhoeffer in 1926.[10] Hydrogen peroxide was found as a product of the low-temperature condensation of electrodissociated water vapor by Lavin and Stewart in 1929,[11] and of an electrodissociated gas mixture of $2H_2 + O_2$ by Brewer and Westhaver in 1930.[12] In 1932, Geib and Harteck discovered that on decomposition of the condensate obtained from the low-temperature reaction of $H + O_2$, not only was hydrogen peroxide produced but also large amounts of gaseous oxygen.[13]

In 1940, Ohara suggested that oxygen evolution and hydrogen peroxide formation upon warming the condensates, obtained from dissociated water vapor and by $H + O_2$ reaction, were due to the decomposition of hydrogen tetroxide, $H_2O_4 \rightarrow H_2O_2 + O_2$, which is stable only at low temperatures.[14] For these condensates the molar ratio of O_2/H_2O_2 in the decomposition products was less than unity. This could be interpreted by assuming that the condensates contained H_2O_4 as well as H_2O_2 and H_2O.

Kobozev et al.[15] were the first to synthesize peroxy radical condensates by reaction of hydrogen atoms with liquid ozone. The molar ratio of O_2/H_2O_2 in its decomposition products was equal to unity, which is distinct from the condensates obtained by other methods, and this ratio was later confirmed by others.[16] Magnetic susceptibility measurements of the condensate showed that it did not contain occluded oxygen; oxygen was only formed during decomposition at elevated temperatures.[17] These results were taken as evidence that the condensate synthesized by $H + O_3(l)$ contained only H_2O_4 and water.

However, subsequent investigations of the condensates obtained from electrodissociated hydrogen/oxygen mixtures have shown that, under certain conditions, the molar ratio of O_2/H_2O_2 in their decomposition products can be as high as 10:1 and even higher.[18] These facts show that the condensate could contain H_2O_3; on warming, H_2O_3 decomposes according to the reaction $H_2O_3 \rightarrow H_2O + O_2$. All the information on the subject leads to the conclusion that the condensates contain not only H_2O_4 but also H_2O_3, and H_2O_3 can be the predominant component.

Vibrational spectroscopy is the most suitable method for detection of the active components in the condensates and their structure determination. Some new bands in the IR spectra of condensates were first observed by Yagodovskaya and Nekrasov,[19] which were tentatively assigned to H_2O_4 and H_2O_3. The first convincing evidence for the presence of H_2O_3 in the peroxy radical condensates was found by Giguère et al.[20,21] They reported fundamental vibrations of the oxygen framework in H_2O_3 by studying IR and Raman spectra of the condensates.

Detailed spectroscopic characterization of H_2O_3 has been performed only recently. Engdahl and Nelander observed all the fundamental vibrations of HOOOH isolated in an Ar matrix, and their experimental results agree very well with the theory.[22] Suma et al. determined the precise geometrical structure of H_2O_3 in the gas phase using advanced Fourier transform microwave spectroscopy techniques.[6] Considerable progress has also been made in studying the H_2O_3 formation in reactions of ozone with organic compounds[3] or hydrogen peroxide[2] in organic solvents. H_2O_3 has been detected by ^1H and ^{17}O NMR spectroscopy.

Giguère et al. did not succeed in observing the true set of HOOOOH oxygen framework fundamental vibrations for H_2O_4, which is discussed below. Subsequent attempts to obtain H_2O_4 in a low-temperature matrix and to characterize the polyoxide by IR spectroscopy were not successful. Tso and Lee[23] tried to prepare HOOOOH by photolysis of formaldehyde or glyoxal in an O_2 matrix at 15 K. The primary products of the photooxidation are two $HO_2^{\cdot}$ radicals and one or two CO molecules. In the secondary reaction, the $HO_2^{\cdot}$ radicals do not give HOOOOH but a cyclic dimer $(HO_2)_2$, which complexes with CO as determined by IR spectroscopy.[23] This conclusion was confirmed theoretically by Schaefer et al.[24] Thus, the existence of HOOOOH in low-temperature solids was thrown to doubt.

In this paper we describe the synthesis of condensates containing both H_2O_4 and H_2O_3 in significant amounts. The polyoxides, H_2O_4 in particular, were characterized by Raman spectra of their oxygen frameworks, and the experimental spectra are in good agreement with the results of quantum chemical calculations.

Results and Discussion

The peroxy radical condensates were obtained by low-temperature condensation of O_2 and H_2 gas mixtures dissociated in a low-pressure microwave discharge. Raman spectra of the condensates show new lines (solid arrows), which do not arise from H_2O or H_2O_2 (Figures 1 and 2). As the oxygen content increases in the initial mixture, the new lines become more pronounced (Figure 2). In addition, signals arising from ozone (706, 1039, and 1106 cm^{-1}) and molecular oxygen (1552 cm^{-1}) appear.

Other lines in the spectra of peroxy radical condensates have analogs in the spectrum of hydrogen peroxide (Figure 1).[25] The intense broad band with a maximum at 3180 cm^{-1} corresponds to the stretching oscillations of OH groups bound with hydrogen bonds. The bending oscillations of HOO give rise to the broad signal with a maximum at 1448–1468 cm^{-1}. The combination of HOO bending oscillations reveals itself as a peak with a maximum at 2840 cm^{-1}. In the condensate prepared by codeposition of nondissociated H_2O_2 and H_2O vapors, these two HOO bending lines have frequencies of 1425 and 2830 cm^{-1}, respectively. In pure crystalline H_2O_2, the frequencies are 1385, 1420 and 2760, 2835 cm^{-1}. The broad unresolved shoulder at 40–380 cm^{-1} is in the same region where lattice vibration lines are observed in the spectrum of crystalline H_2O_2. The broad weak signals of fused quartz (from the reactor) may appear in the region 40–550 cm^{-1}.

An intense peak in the neighborhood of 880 cm^{-1} represents the convolution of three signals (Supporting Information). This shows itself particularly well in oxygen-rich gas mixtures where a shoulder at ca. 865 cm^{-1} can be observed.

The shape of the peak near the maximum led us to suspect that there are several signals with heights positioned

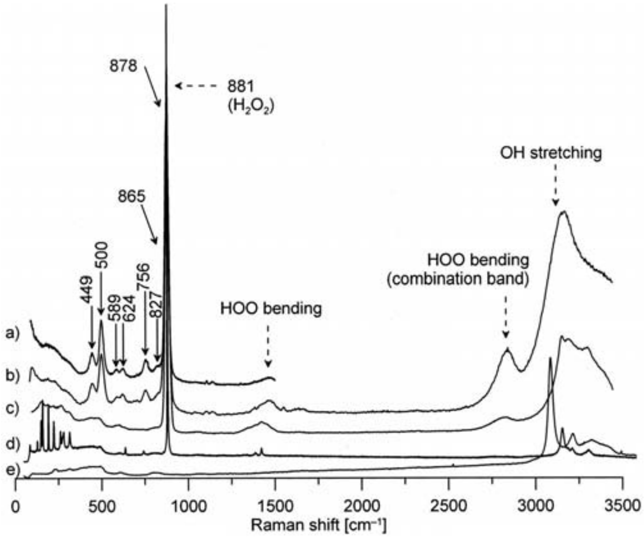

Figure 1. Raman spectra of peroxy radical condensates (a and b) in comparison with Raman spectra of condensates of H_2O_2 (70 mol-%) in water (c), solid crystalline hydrogen peroxide (d), and solid water (e). New lines are marked with solid arrows. The peroxy radical condensate was synthesized from a mixture of 86 vol.-% O_2 and 14 vol.-% H_2. The spectra are normalized with reference to the height of the peak at ca. 880 cm^{-1}, which is taken as 100% (a, b, c, e) or 200% (d).

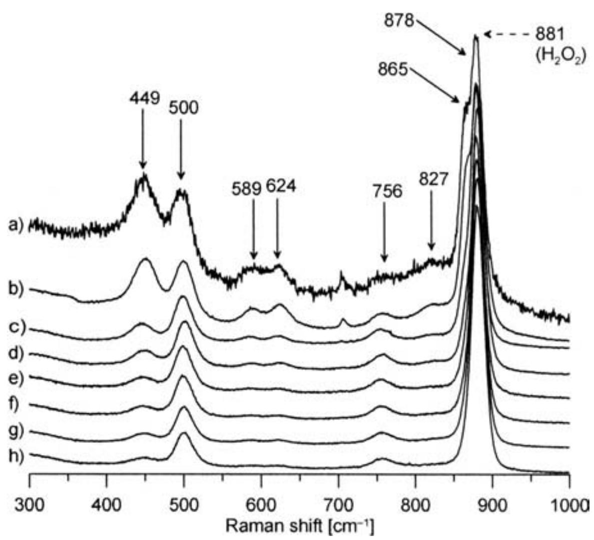

Figure 2. Raman spectra of peroxy radical condensates synthesized from O_2/H_2 mixtures of different compositions. O_2 content in the initial gas mixture in vol.-%: 98.3 (a), 96.6 (b), 86 (c), 80 (d), 70 (e), 60 (f), 50 (g), 33 (h); gas flow rate in L/h (STP, standard temperature and pressure, 20 °C and 1 atm): 3.2 (a, c–h), 1.6 (b). The spectra are normalized with reference to the height of the peak at ca. 880 cm^{-1}.

very close to 880 cm^{-1}. Numerical deconvolution disclosed that the peak is a superposition of three lines with maxima at 865, 878, and 881 cm^{-1} (Supporting Information). The line at 881 cm^{-1} is caused by OO stretching vibrations of H_2O_2. The lines at 865 and 878 cm^{-1} are new and do not have analogs in the H_2O_2 spectrum.

The new lines can be divided into two sets: 500, 756, and 878 cm^{-1} and 449, 589, 624, 827, and 865 cm^{-1}. As the oxygen content increases in the initial mixture, the line intensities of the second set grow more rapidly than those of the first (Figure 2). Within both sets, the intensities change in the same manner.

In order to elucidate whether the new lines correspond to normal vibrations, which include only O atoms or both O and H atoms, the spectra of condensates obtained from $O_2 + H_2$ were compared to those obtained from $O_2 + D_2O$ gas mixtures (Figure 3). The substitution of deuterium for hydrogen does not cause any appreciable shift of the new lines. Therefore, we conclude that the new lines are due to normal vibrations incorporating O atoms only.

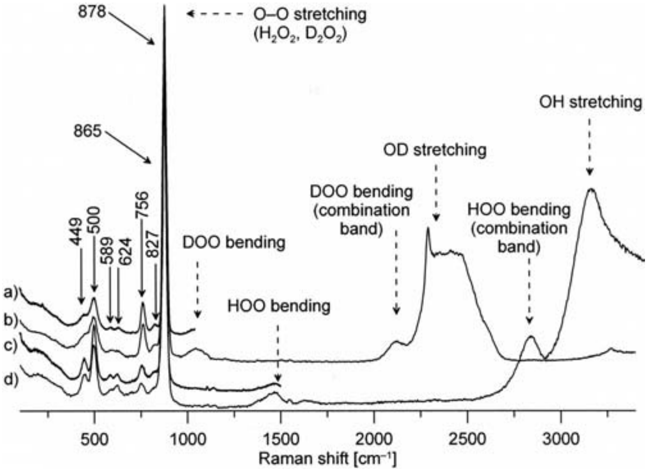

Figure 3. Spectra of the peroxy radical condensates synthesized from oxygen/deuterium (a, b) and oxygen/hydrogen (c, d) systems. Experimental conditions: (a, b) initial gas mixture 70 vol.-% O_2 + 30 vol.-% D_2O [gas flow rate 3.0 L/h (STP)]; (c, d) initial gas mixture 86 vol.-% O_2 + 14 vol.-% H_2. The spectra are normalized with reference to the height of the peak at ca. 880 cm^{-1}.

Thus, the new lines result from compounds of oxygen and hydrogen other than H_2O, H_2O_2, O_2, and O_3. Free radicals, $HO_2^{\cdot}$ in particular, should be virtually "invisible" in the Raman spectra as their concentration in the condensates is low (less than 0.5 wt.-%).[26] $(HO_2)_2$ and isomeric hydrogen peroxide H_2OO can also be excluded from consideration.[27] It is likely that the new lines arise from H_2O_4 and H_2O_3.

In order to assign the new lines correctly, quantum chemical calculations for the vibrational spectra of hydrogen peroxide (HOOH) and polyoxide (HOOOH, HOOOOH) molecules were performed. The density functional method B3LYP/6-31+G(d,p) was employed (Supporting Information).[28] The calculations were carried out for isolated molecules in an ideal gaseous state. The experimental Raman spectra were taken from glassy solid condensates with strong hydrogen bonding. Evidently, the matrix exerts a strong influence on oscillations including hydrogen atoms and much less influence on oxygen framework oscillations. For this reason, comparison of the calculated and experimental frequencies makes sense only for oxygen framework oscillations. The calculated frequencies were scaled in a way that the calculated frequency of the H_2O_2 OO stretching vibration (unscaled value 921 cm^{-1}) was equal to its experimental value (881 cm^{-1}) in solid hydrogen peroxide.

A comparison of the experimental condensate spectrum and the calculated Raman spectra of HOOH, HOOOH, and HOOOOH is given in Figure 4 and Table 1. The first set of new lines is consistent with the three skeletal vibrations of hydrogen trioxide. The second set corresponds to the vibrations of the hydrogen tetroxide oxygen framework. However, the second set comprises only five lines when there are six skeletal vibrations of H_2O_4. The line arising from the O_4 torsion vibration does not manifest itself in the experiment. This was expected, because – according to the calculations – this line and the lines of the other torsion oscillations of H_2O_2, H_2O_3, and H_2O_4 are of low Raman intensity and fall in the region of the rather strong broad unresolved signal ("shoulder") at 50–400 cm^{-1}. This shoulder is present in all of our spectra and obscures the O_4 torsion line.

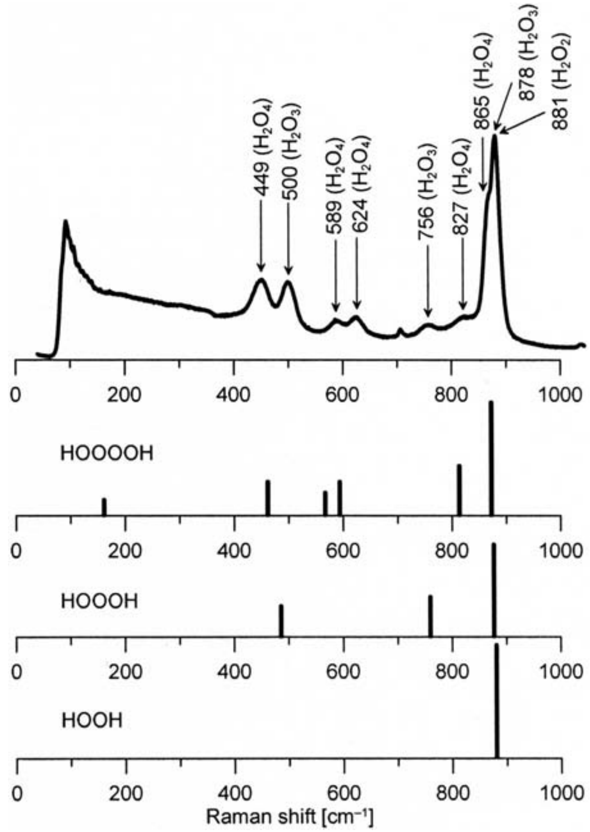

Figure 4. Experimental Raman spectrum of the peroxy radical condensate and calculated Raman spectra of hydrogen tetroxide, hydrogen trioxide, and hydrogen peroxide in the range of the oxygen framework vibrations. The spectra are normalized with reference to the height of the peak at ca. 880 cm^{-1}. The condensate was synthesized from the initial gas mixture 96.6 vol.-% O_2 + 3.4 vol.-% H_2 [gas flow rate 1.6 L/h (STP)].

On the whole, the experimental spectrum in the region 350–1000 cm^{-1} represents the superposition of the lines of the oxygen framework oscillations of HOOH, HOOOH, and HOOOOH. The most intense signal in the vicinity of 880 cm^{-1} is superimposed by the lines of the symmetric O–O stretching vibrations of H_2O_2 (881 cm^{-1}), H_2O_3 (878 cm^{-1}), and H_2O_4 (865 cm^{-1}). The lines of other oxygen framework oscillations are clearly separated. The calculated spectra fit those obtained experimentally fairly well (Figure 4). The difference in line positions is not principal, because the strong intermolecular interactions in the condensate were not taken into account in the calculations.

Denis and Ornellas[29] have calculated the vibrational spectra of H_2O_3 and H_2O_4 at higher levels of theory [CCSD(T)/cc-pVTZ and B3LYP/6-311+G(3df,2p)], but Raman intensities have not been reported. The CCSD(T) methodology gives the frequencies closest to the experimental values obtained in this work. The frequencies obtained by B3LYP methods are systematically higher than those observed experimentally, which is due to methodological reasons, but the performance of these methods is still good. Our frequencies (unscaled) calculated with the 6-31+G(d,p) basis set are closer to the experimental results than those obtained with the 6-311+G(3df,2p) basis set.[29]

In addition to this work, the vibrational spectrum of H_2O_3 and H_2O_4 in a peroxy radical condensate was reported by Giguère et al.[20,21] (see Table 1 for a comparison of the frequencies). For H_2O_3, the asymmetric OO stretching (755 cm^{-1}) and OOO bending (500 cm^{-1}) frequencies coincide with our values. However, the shoulder signal at ca. 855 cm^{-1}, which Giguère et al. assigned to the H_2O_3 symmetric OO stretching vibration, is in fact due to the analogous vibration of H_2O_4. Its frequency is equal to 865 cm^{-1} in our experiments. The line of the symmetric OO stretching vibration of H_2O_3 is at 878 cm^{-1} and is visually almost indistinguishable from that of H_2O_2 at 881 cm^{-1}. The lines at 865 and 878 cm^{-1} were identified by the numerical deconvolution of the peak at ca. 880 cm^{-1} as mentioned above.

Giguère et al.[20,21] observed with certainty only two oxygen framework lines for H_2O_4 with frequencies of 820–830 and 450 cm^{-1} in their experiment. This is because their condensates contained less than 0.6% of this polyoxide.[30] Other frequencies were assumed based on rather unclear experimental signals and by analogy with the vibrational spectra of the homological series of hydrogen polyoxides and polysulfides. As a result three (out of six) frequencies assigned by Giguère et al.[21] to H_2O_4 skeletal oscillations disagree with our new experimental and theoretical values and with the theoretical frequencies of Denis and Ornellas.[29] We were able to prepare condensates that contained up to 20% of H_2O_4, which allowed us to characterize its vibrational spectrum in greater detail.

Estimates of the composition of the peroxy radical condensates are presented in Figure 5 (see Exp. Sect. for the composition determination procedure). At an oxygen content of 60–70%, the prevailing condensate components are H_2O_2 and H_2O_3. The largest amount of H_2O_3 in the condensate was 30%, which was attained when the initial gas mixture contained 70% O_2. With an increased oxygen ratio in the initial gases, the H_2O_2 and H_2O_3 content decreased and that of H_2O and H_2O_4 increased. The condensate prepared from 98% O_2 and 2% H_2 had the highest concentra-

Table 1. Frequencies of fundamental vibrations of H_2O_3 and H_2O_4 oxygen frameworks [cm^{-1}].

Approximate normal mode[a]	This work, experimental	Giguère et al.,[b,c] experimental	Engdahl and Nelander,[d,e] experimental	This work, calculated B3LYP/6-31+G(d,p), scaled	This work, calculated B3LYP/6-31+G(d,p), unscaled	Denis and Ornellas,[29] calculated, B3LYP/6-311+G(3df,2p)	Denis and Ornellas,[29] calculated, CCSD(T)/cc-pVTZ
HOOOH							
Symm OO stretch	878	ca. 855	821.0	878	917	925	879
Asym OO stretch	756	755	776.3	760	795	795	784
OOO bend	500	500	509.1	486	508	516	508
HOOOOH							
Symm OO stretch	865	ca. 855		873	912	922	882
Asym OO stretch	827	ca. 823		814	851	847	833
Center OO stretch	624	ca. 764		594	621	629	672
OOO bend 1	589	(435)		567	593	607	601
OOO bend 2	449	450		462	483	479	470
O_4 torsion	–	ca. 98		162	169	172	166

[a] The descriptions of H_2O_4 normal modes in this work and in refs.[21,29] are somewhat different. [b] The values are from the closing work,[21] which is based on the experimental results from refs.[20] [c] One should consult the paper by Giguère at al.[21] with regard to obtaining and assigning the frequencies. For H_2O_4, only the peaks at 450 and ca. 823 cm^{-1} were clearly observed. [d] Experimental values from ref.[22] The authors[22] observed the complete set of nine HOOOH fundamental oscillations, and not just oxygen framework fundamentals. [e] The difference between the frequencies reported in this work and by Engdahl and Nelander[22] is most likely to result from the different environments in the two cases. In this work H_2O_3 was synthesized as a component of peroxy radical condensates, which consist of H_2O, H_2O_2, H_2O_3, and H_2O_4 in comparable quantities, with strong intermolecular interactions between the constituents. Engdahl and Nelander prepared H_2O_3 isolated in an Ar matrix with virtually no intermolecular interactions.

tion of H_2O_4 (20%), although its main component was H_2O (55%). The absolute quantity of condensate in our experiments was about 20 mmol. Therefore, condensates with relatively high contents of H_2O_3 and H_2O_4 have been prepared. This made it possible to perform an experimental determination of the important properties of the polyoxides, such as their heat of decomposition.

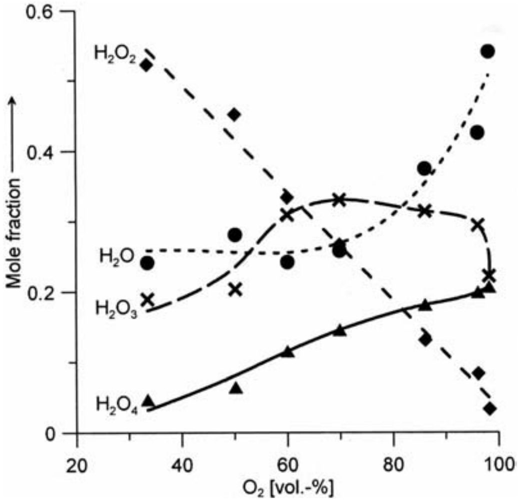

Figure 5. Composition of the peroxy radical condensate vs. O_2 content in the initial gas mixture O_2/H_2.

Conclusions

Hydrogen polyoxides were prepared in relatively large quantities as components of peroxy radical condensates. The polyoxides were characterized by the vibrational Raman spectra of their oxygen frameworks. The lines at 500, 756, and 878 cm^{-1} correspond to skeletal oscillations of H_2O_3 in the condensate (OOO bend, asymmetric OO stretch, symmetric OO stretch). The lines at 449, 589, 624, 827, and 865 cm^{-1} match the skeletal vibrations of H_2O_4 (OOO bend 1, OOO bend 2, center OO stretch, asymmetric OO stretch, symmetric OO stretch). The O_4 torsion vibration of hydrogen tetroxide was not observed experimentally. According to the data available in the literature, this work is the first to report the preparation of H_2O_4 in a significant concentration and describe its Raman spectrum.

Experimental Section

General: Peroxy radical condensates were synthesized from oxygen/hydrogen gas mixtures of different compositions and from D_2O vapor/O_2 mixtures, dissociated at low pressure (0.85–1.0 Torr) by electrodeless microwave discharge. The experimental setup was essentially a conventional discharge-flow system with a low-temperature reactor-cryostat filled with liquid nitrogen. The condensate was formed on the cryostat "finger". Immediately after the synthesis, the condensate was investigated in situ by Raman spectroscopy. The condensate was decomposed by heating, with the formation of gaseous O_2 and liquid H_2O_2 solution in water. The oxygen evolved was measured manometrically. The H_2O_2 solution was weighed, the amount of H_2O_2 was determined by titration with $KMnO_4$, and the amount of water by difference. The condensate composition was determined from the amounts of the decomposition products and the relative intensities of the H_2O_3 and H_2O_4 peaks in the Raman spectra. A detailed description of the procedures is given below.

Experimental Setup and Procedure: The low-temperature reactor is shown in Figure 6. The outer part of the reactor was made of fused quartz of optical quality. The inner cryostat ("finger"), was made of glass, and its bottom was a polished stainless steel conical cap. The cap was soldered to the Kovar junction welded with glass. The cryostat was filled with liquid nitrogen at 77 K. The parts of the reactor were connected by ground conical joints. Apiezon grease M was used on all the joints and stopcocks of the setup.

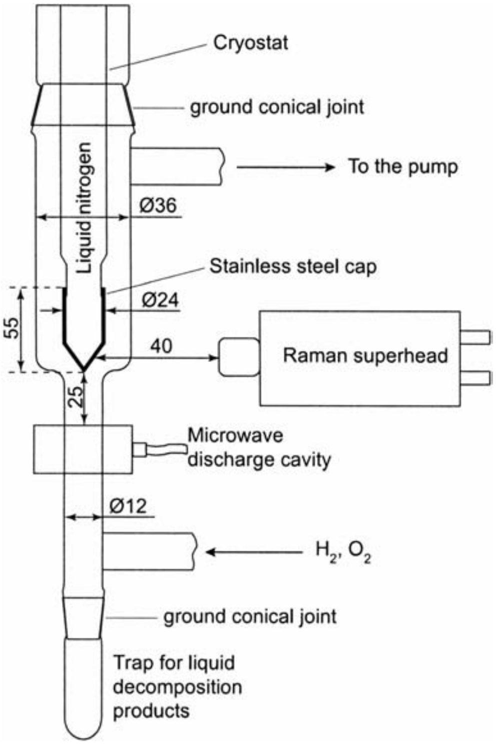

Figure 6. Reactor for the synthesis of peroxy radical condensates and their investigation by Raman spectroscopy.

The setup was pumped with Vacfox VC-75 and GLD-201 vacuum pumps. The input gases (very high purity grade) were taken from cylinders with pressure regulators and conducted to the setup through calibrated capillaries. The gas flow rates were regulated by varying pressure at the capillary inlets. The setup was furnished with a thermostatted vaporizer for admission of H_2O or D_2O vapors into the reactor. The overall gas flow rate was 3.2 L/h (STP) in nearly all experiments, unless otherwise noted.

The pressure during the synthesis was controlled by a differential manometer filled with vacuum pump oil (density 0.88 g/cm^3), and took values between 0.85 and 1.0 Torr. The pressure during the condensate decomposition was measured with an AIR-20/M2 electronic pressure gauge connected to a computer.

The discharge was sustained by a Luch-11 (2450 MHz) medical microwave generator, whose nominal output power was 12 W in O_2/H_2 mixtures and 42 W in the O_2/D_2O mixture. The design of the microwave discharge cavity was similar to that described by Broida et al.[31] (type 5).

Before the synthesis, the gas flow rates were set, and the discharge was initiated. The reactor "finger" was filled with liquid nitrogen, and the synthesis started. The gas mixture passed through the discharge and dissociated before it flew onto the cold finger cap where the peroxy radical condensate was formed in reactions of active particles from the gas phase. The duration of the synthesis was 1.5–5 h.

When the synthesis was complete, the condensate was investigated in situ by Raman spectroscopy. The spectra were recorded with a Horiba Jobin Yvon LabRam HR 800 UV spectrometer (diffraction grating 1800 or 300 lines/mm) equipped with an external sensing unit ("superhead"). Green radiation (514.532 nm) from an ion argon laser was employed for excitation with the power at the sample of 20 mW and the exposure time of about 100 s. All the spectra were measured at one definite point on the finger cap surface, located at the half-height of the cone. Numerical deconvolution of peaks in the Raman spectra was performed with the PeakFit 4.12 program.[32]

Analysis of Decomposition Products: After Raman investigation, liquid nitrogen was removed from the cryostat and the reactor heated up to room temperature. The condensate decomposed to O_2 and aqueous hydrogen peroxide solution. The oxygen evolved was measured by its pressure in a known volume. Before the decomposition, a known amount of dry gaseous oxygen was admitted into the setup. This approach ensured that the evaporation of H_2O and H_2O_2 was negligible. The total pressure was recorded over the entire course of the decomposition with the electronic pressure gauge until the setup reached room temperature. The pressure of the oxygen evolved was deduced from the total pressure vs. time curve.

At high oxygen content in the initial gas mixture, the condensates contained quantities of ozone and occluded molecular oxygen. As a rule, these quantities were negligible compared to the main components. Only when the oxygen content was more than 95% did they become appreciable. On warming the condensate, ozone and occluded molecular oxygen were the first to be released into the gas phase, and the molecular oxygen formed in the breakdown of H_2O_3 and H_2O_4 was subsequently evolved. This allowed us to separate these gases with some degree of certainty. In this work the composition of condensates is given without the content of ozone and occluded molecular oxygen.

The liquid decomposition products (H_2O_2 and H_2O) were collected in a special trap and remained on the reactor walls. The trap was weighed, the amount of H_2O_2 in the trap was determined by titration with potassium permanganate according to a standard technique,[33] and the amount of H_2O was determined by difference. The reactor walls were rinsed with distilled water, and the amount of H_2O_2 on the walls was also determined by titration. The amount of H_2O on the walls was estimated from the ratio of H_2O_2/H_2O in the trap. This procedure enabled all the condensate decomposition products to be determined.

Determination of Peroxy Radical Condensate Composition: The main components of the peroxy radical condensates were H_2O, H_2O_2, H_2O_3, and H_2O_4. Their content in the condensates was evaluated from the amounts of condensate decomposition products (O_2, H_2O, H_2O_2) and the relative intensities of the H_2O_3 and H_2O_4 peaks at 500 and 449 cm^{-1} in the Raman spectra of the condensates. The following relationships hold true:

$$n(H_2O) + n(H_2O_3) = N_{H_2O},$$

$$n(H_2O_2) + n(H_2O_4) = N_{H_2O_2},$$

$$n(H_2O_3) + n(H_2O_4) = N_{O_2},$$

$$n(H_2O_4)/n(H_2O_3) = a \cdot I_{449}/I_{500},$$

where $n(H_2O)$, $n(H_2O_2)$, $n(H_2O_3)$, and $n(H_2O_4)$ are the quantities of the condensate components, N_{H_2O}, $N_{H_2O_2}$, and N_{O_2} are the quantities of the decomposition products, I_{449} and I_{500} are the peak areas, and a is a calibration coefficient. The value $a = 0.92$ was estimated on the basis of the theoretical Raman intensities of the corresponding lines, calculated in this work. The relationships represent a nondegenerate system of linear equations whose solution gives the composition of the condensate. The results of the composition determination are not highly precise. The main reasons are that: (1) the weight of liquid decomposition products was determined with a relative error of 3–10%, (2) at an O_2 content in the initial gas mixture of more than 95%, ozone and occluded molecular oxygen in the condensate interfere with the determination of the quantity of molecular oxygen evolved on condensate decomposition, and (3) the condensate composition is nonuniform along its height.

Supporting Information (see footnote on the first page of this article): Illustration of the deconvolution of the composite peak at approximately 880 cm^{-1} in the Raman spectra of peroxy radical condensates; description of the calculation methods; optimized structures for HOOH, HOOOH, HOOOOH calculated in this work.

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[27] In principle, H_2OO (isomeric hydrogen peroxide, oxywater) and $(HO_2)_2$ (cyclic dimer of the $HO_2^{\cdot}$ radical) should be taken into account as possible components of peroxy radical condensates. However, the calculated vibrational spectra available from the literature allow us to exclude these compounds from consideration. Indeed, the vibrational spectrum of H_2OO should have only one band due to oxygen framework oscillations (harmonic frequency 665 cm^{-1}) (H. H. Huang, Y. Xie, H. F. Schaefer III, *J. Phys. Chem.* **1996**, *100*, 6076–6080). The spectrum of $(HO_2)_2$ should have three Raman-active oscillations (harmonic frequencies 1233, 230, 182 cm^{-1}) whose frequencies do not essentially change on substitution of deuterium for hydrogen (J. T. Fermann, B. C. Huffman, G. S. Tschumper, H. F. Schaefer III, *J. Chem. Phys.* **1997**, *106*, 5102–5108). Lines with these features are not present in our spectra.

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