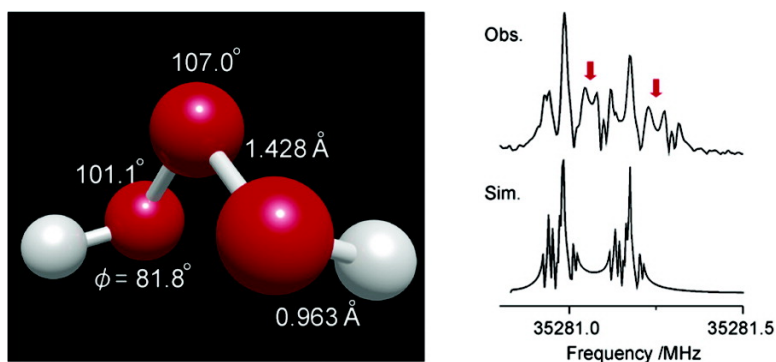


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## The Rotational Spectrum and Structure of HOOH

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Hydrogen oxides,  $\text{H}_2\text{O}_n$  with  $n = 1$  (i.e., water) and  $n = 2$  (i.e., hydrogen peroxide), are familiar species in various fields of natural science. However, extended species ( $n > 2$ ), namely, hydrogen polyoxides, have been believed to be quite unstable due to the repulsion between the lone-pair electrons on the oxygen atoms. Thus, the questions, "how long can you make an oxygen chain?" and "if such oxygen chain molecules exist, what kind of roles do these molecules play?" have long been fascinating chemists even from the 19th century.<sup>2</sup> Recently, we have reported a microwave observation of a radical species with three oxygen atoms,  $\text{HO}_3$ , and determined its precise molecular structure.  $\text{HO}_3$  is regarded as a weak adduct of  $\text{HO}-\text{O}_2$  and is expected to be a sink of the atmospheric OH radical.<sup>3</sup> On the other hand, no detection of a closed shell species,  $\text{H}_2\text{O}_3$ , in the gas phase has been reported yet. Its existence and stability in the gas phase, as well as its precise molecular structure, are still open questions. Recent theoretical studies predict its existence in the gas phase. For example, McKay et al. predicted that the oxygen chain could be extended infinitely in a very low temperature gas.<sup>1</sup> Several experiments on  $\text{H}_2\text{O}_3$  in the condensed phase have meanwhile been reported. Infrared absorption spectra in a solid state<sup>4</sup> and the Ar matrix<sup>5</sup> and NMR spectra in several organic solutions<sup>6</sup> have shown its existence in respective media. These reports indicate that  $\text{H}_2\text{O}_3$  is far more stable than was previously believed. Plesničar et al. have recently reviewed these experiments.<sup>6</sup>

Wentworth et al. reported that all antibodies were capable of catalyzing the oxidation of water by singlet oxygen ( $^1\Delta \text{O}_2$ ) to generate  $\text{H}_2\text{O}_2$  and probably  $\text{O}_3$ , as well, and postulated that these antibodies carry the reaction through  $\text{H}_2\text{O}_3$  as a key intermediate.<sup>7</sup> Furthermore,  $\text{H}_2\text{O}_3$  is expected to be involved in oxidation processes that span atmospheric, environmental, and biological systems.<sup>6</sup> It is thus expected that precise rotational transitions could be used to probe  $\text{H}_2\text{O}_3$  and to elucidate its potential roles in these chemical systems, if they are observed.

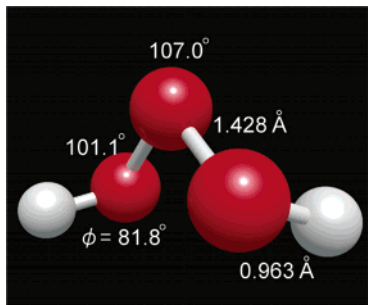
In the present study, we were able to detect  $\text{H}_2\text{O}_3$  by Fourier transform microwave (FTMW) spectroscopy<sup>8</sup> and FTMW-mm-wave double resonance<sup>9</sup> and triple resonance spectroscopy, providing sufficient data to precisely determine its ground-state geometry.  $\text{H}_2\text{O}_3$  was produced in a pulsed discharge nozzle (PDN) by discharging a gas mixture of  $\text{O}_2$  (10%) and Ar, passed through a reservoir filled with a 30% hydrogen peroxide solution. Discharged products were expanded as a supersonic jet into a FTMW spectrometer cavity. Since  $\text{H}_2\text{O}_3$  is a singlet molecule without any hyperfine splittings and only one component of the dipole moment,  $\mu_b$ , has a nonzero value in the *trans* form ( $C_2$  symmetry), the observable transition by our FTMW spectrometer, whose frequency coverage is 4–40 GHz, is limited to only one,  $3_{03} - 2_{12}$ , at about 21 GHz, which was predicted by an ab initio calculation.<sup>10–12</sup> Therefore, we performed double resonance spectroscopy by monitoring all possible candidate lines observed in the region of  $21 \pm 2$  GHz, to check which of the lines belongs to  $\text{H}_2\text{O}_3$ . The lines to

be checked by double resonance spectroscopy were selected beforehand to a few lines by checking if they show a diamagnetic behavior, are the discharge products, need both hydrogen peroxide and  $\text{O}_2$ , and do not depend on a particular buffer gas, Ar or Ne. When one of the observed lines at 20 838.6 MHz was used as a monitor for  $3_{03} - 2_{12}$ , double resonance signals at the predicted regions, 45 ( $3_{12} - 3_{03}$ ), 79 ( $2_{12} - 1_{01}$ ), and 186 ( $3_{21} - 2_{12}$ ) GHz, were observed. For the confirmation of the spectral carrier, a newly developed triple resonance method was also applied to observe the transition,  $1_{10} - 1_{01}$ , at 42 GHz. Details of this technique will be reported elsewhere. In total, five rotational transitions, as shown in Supporting Information, were observed. Neither *a*-type nor *c*-type transitions were observed around the predicted frequencies, indicating that the dipole moment components,  $\mu_a$  and  $\mu_c$ , are 0 or very small. These results support that the spectral carrier is  $\text{H}_2\text{O}_3$  in the *trans* form. We could not observe transitions of the *cis* isomer ( $C_s$  symmetry) despite careful scans with similar experimental conditions in sufficiently wide frequency regions. The transition at 20 838.6 MHz was also observed slightly weakly by discharging a mixture gas of  $\text{H}_2\text{O}/\text{O}_2/\text{Ar}$ . Rotational transitions of  $\text{D}_2\text{O}_3$  were thus searched for by using the  $\text{D}_2\text{O}/\text{O}_2/\text{Ar}$  mixture gas. Three transitions listed in the table in Supporting Information were observed by FTMW spectroscopy. Using these transitions as monitors, two more transitions were observed by the double resonance technique. In total, five rotational transitions were observed for  $\text{D}_2\text{O}_3$ . Although the dipole moments,  $\mu_b$ , of  $\text{H}_2\text{O}_3$  and  $\text{D}_2\text{O}_3$  are almost identical—about 1 D predicted by B3LYP/cc-pVQZ calculations<sup>10</sup>—signals of  $\text{D}_2\text{O}_3$  were much weaker than expected from those of  $\text{H}_2\text{O}_3$ . By irradiating the microwave parallel to the supersonic jet beam,<sup>13</sup> small hyperfine splittings due to the electric quadrupole moment of deuterons were resolved. Since  $\text{D}_2\text{O}_3$  has two equivalent deuterons, which obey Bose–Einstein statistics, the rotational energy levels consist of ortho ( $I_{\text{total}} = 0, 2$ ) and para ( $I_{\text{total}} = 1$ ) states. The  $1_{10} - 1_{01}$  transition (para) is well reproduced by the electric quadrupole coupling constants obtained by the ab initio calculation.<sup>10</sup>

However, extra lines were observed for two other transitions  $3_{03} - 2_{12}$  and  $2_{11} - 2_{02}$ , as shown in the figures in Supporting Information. They were observed for both ortho and para states and could not be explained by changing the values of the electric quadrupole coupling constants within a reasonable range. On the other hand, no such doubling was observed for  $\text{H}_2\text{O}_3$ . At present, we were not able to explain the origin of these splittings. They could be considered to be the splittings caused by the tunneling between the two chiral isomers through the torsional motions of OH moieties. However, these splittings are estimated to be extremely small by the simple WKB (Wentzel–Kramers–Brillouin) approximation along the one-dimensional torsion vibration coordinate using a potential energy surface obtained by the B3LYP/cc-pVTZ calculation.<sup>10</sup>  $\text{H}_2\text{O}_3$  should be considered to be a chiral molecule at the time scale of our experimental apparatus, and no tunneling splittings should be observed. Although parity-violation effect may also

**Table 1.** Comparison of the Rotational Constants of the *cis* and *trans* Forms Obtained by the Ab Initio Calculation with Those Determined Experimentally (in MHz)

	HOOOH			DOOOD		
	<i>cis</i>	<i>trans</i>	exp.	<i>cis</i>	<i>trans</i>	exp.
$A_0$	52437	51152	51149	44287	42962	43043
$B_0$	10558	10719	10688	9549	9740	9709
$C_0$	9297	9380	9355	8646	8770	8745



**Figure 1.** The molecular structure of HOOOH determined from the experimental rotational constants and the vibration–rotation constants derived by the ab initio calculations. The structural parameters predicted by the ab initio calculations are  $r_{OH} = 0.966 \text{ \AA}$ ,  $r_{OO} = 1.427 \text{ \AA}$ ,  $\theta(OOO) = 107.0^\circ$ ,  $\theta(HOO) = 101.1^\circ$ , and  $\varphi(HO-OO) = 81.1^\circ$  (dihedral angle).

contribute to these splittings, such an effect is too small for the splittings to be ascribed to this effect. Clarification of these mysterious splittings requires more extensive experimental studies along with more accurate theoretical studies.

Five molecular constants listed in Supporting Information have been directly determined from the observed five transitions for each isotopomers by using Watson's *A*-reduced Hamiltonian, where the hyperfine splittings of  $D_2O_3$  were neglected. The standard deviations in the least-squares analysis become larger than the experimental accuracy, if all of the centrifugal distortion constants are fixed to the ab initio values.<sup>10</sup> The negative nonzero inertial defects,  $\Delta I = I_{cc} - I_{bb} - I_{aa} = -3.143 \text{ u\AA}^2$  for  $H_2O_3$  and  $\Delta I = -6.007 \text{ u\AA}^2$  for  $D_2O_3$ , clearly suggest  $H_2O_3$  is nonplanar. The rotational constants agree well with those of the *trans* form predicted by the ab initio calculation, as shown in Table 1, where the ab initio rotational constants are corrected for the vibration–rotation constants.<sup>10</sup> Differences of the rotational constants predicted for the *trans* form are less than 1%. These agreements are reasonable for typical singlet molecules and support that the observed  $H_2O_3$  is in the *trans* form.

By assuming  $H_2O_3$  is in a *trans* geometry, the molecular structure shown in Figure 1 was determined from the rotational constants of  $H_2O_3$  and  $D_2O_3$ , whose vibration–rotation constants were corrected by the ab initio calculation.<sup>10</sup> The O–O bond lengths of  $H_2O_3$ , 1.428 Å, are much shorter than that of the radical species, (HO–OO), 1.688 Å,<sup>3</sup> and are even shorter than that of  $H_2O_2$ , 1.464 Å.<sup>14</sup> This fact clearly indicates that, although the  $HO_3$  radical can be regarded as a weakly bound HO–OO adduct,  $H_2O_3$  is a molecule with rigid O–O bonds, which are stronger than that of  $H_2O_2$ . The determined molecular structure agrees very well with that of the ab initio calculation. This situation is also quite different from the case of HOOO, where results deviate significantly depending on the calculation methods employed.<sup>3</sup>

The present microwave data provide us means for its detection in the earth's atmosphere and, conceivably, in the interstellar space. For example, the observed transition frequency of  $H_2O_3$ , 20838.6 MHz, agrees well with the U-line (20 838.2 MHz) observed in the W51 region.<sup>15</sup> Both HOOOH and HOOO<sup>3</sup> are considered to be the starting point species for the investigations of the chain formation ability of the oxygen atom. Their successful detections by the high-resolution spectroscopic method in the gas phase have now firmly established the stabilities of the  $H_nO_3$  ( $n = 1, 2$ ) systems and opened a possibility to investigate the existence and detection of other catenated oxygen species. For example, observations of the rotational transitions of species such as  $H_2O_4$ <sup>2</sup> and XOOOH (X = halogen,<sup>16</sup> methyl,<sup>17</sup> and so on) are well expected by a similar experimental setup. Such observations should reveal their accurate and detailed characters and give means for the detections in various chemical systems. These studies will lead us to the chemistry of "oxygen chain molecules".

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**Supporting Information Available:** Complete refs 11 and 12 and observed and simulated microwave spectra of  $D_2O_3$  and rotational transition frequencies, molecular constants, and energy diagrams of  $H_2O_3$  and  $D_2O_3$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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